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The Lengths of the Links of Unsaturated Hydrocarbon Molecules

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The lengths of the links in conjugated chain molecules $C_{2n}H_{2n+2}$ and in condensed aromatic hydrocarbons such as benzene, naphthalene and diphenyl are calculated on the assumption that there is a simple interaction energy between all contiguous carbon-carbon bonds. The lengths thus deduced are in excellent agreement with those determined by the use of quantum-mechanical ideas of resonance.

IT is known that the links in many unsaturated hydrocarbons (e.g. benzene C_6H_6 or butadiene C_4H_6) have lengths which are neither those of a pure single bond nor of a pure double bond, but which are, in general, intermediate between the two. The author has recently shown[1] how these lengths may be calculated if we assume that certain of the electrons (the π- or mobile electrons) are able to move through the molecule in a manner similar to the conduction electrons of a metal. Alternatively[2] the calculations may be made, with similar results, using the valence-bond method of Pauling.

These calculations, however, are extremely cumbersome, and in this note we shall show how the various lengths may be obtained without much difficulty, using an empirical expression for the energy of interaction between each pair of consecutive links.

In the unsaturated hydrocarbons, the three bond directions are inclined at angles of approximately 120° and lie in a plane; they are the trigonal bonds of Pauling.[3] We may regard the process of building up one of these molecules as consisting of two stages; first we "excite" the individual carbon atoms into the trigonal state, and second we allow these excited atoms to interact among themselves. We shall, as usual, neglect the effect of the C−H bonds in this discussion; this does not mean that their presence has no effect upon the rest of the molecule, but we do, in fact, here assume that they merely add a constant amount to the energy. The second stage, therefore, consists solely in discussing the mutual interactions of a number of such trigonal, or aromatic, carbon atoms.

The natural length of a trigonal bond, when no other similar bonds are present (e.g. ethylene), is 1.330A.[4] Thus, if we write $a=1.330$A, and choose our zero and unit of energy suitably, then the energy of such a bond, when its length is x, may be written

$$E=(x-a)^2. \qquad (1)$$

A more complete analysis, especially in those cases where the lengths differ greatly from the value a, would demand the use of a Morse func-

[1] (a) Coulson, Proc. Roy. Soc. **A169**, 413 (1939); (b) Lennard-Jones and Coulson, Trans. Faraday Soc. **35**, 811 (1939).
[2] Penney, Proc. Roy. Soc. **A158**, 306 (1937).
[3] Pauling, J. Am. Chem. Soc. **53**, 1367, 3225 (1931).

[4] Recent work of Thompson, Trans. Faraday Soc. **35**, 697 (1939), suggests 1.331A for the C=C bond in ethylene. But 1.330 is within his probable error, and this value facilitates comparison with the results of reference 1.

TABLE I. *Lengths of links in conjugated chains* $C_{2n}H_{2n+2}$.

Molecule	n	Link 1		Link 2		Link 3		Link 4	
		Pres. Paper	Reson.	Pres. Paper	Reson.	Pres. Paper	Reson.	Pres. Paper	Reson.
Ethylene	1	1.330	1.330	—	—	—	—	—	—
Butadiene	2	1.347	1.347	1.432	1.432	—	—	—	—
Hexatriene	3	1.352	1.351	1.419	1.424	1.375	1.366	—	—
Octatetraene	4	1.349	1.353	1.425	1.422	1.376	1.371	1.400	1.415

tion instead of (1), but since we are chiefly interested in qualitative values, we shall adhere to the simpler expression.

When there are several trigonal bonds present, there will be an interaction between them (one way of describing this interaction is to say that there is "resonance"), and we shall have an interaction energy. To the same accuracy that the parabolic law (1) is valid, we may expect the contribution to this energy arising from a pair of contiguous links x_1 and x_2, to be expressible[5] in the form

$$2bx_1x_2+2c(x_1+x_2). \tag{2}$$

The total energy $E(x_1x_2\cdots x_n)$ of these links in a molecule is then the sum of terms (1) from each trigonal bond, and terms (2) from each pair of links with a common carbon atom. The equilibrium values of x_1, x_2, $\cdots$ are those which minimize E and hence satisfy the "defining equations"

$$\partial E/\partial x_1=\partial E/\partial x_2=\cdots=\partial E/\partial x_n=0. \tag{3}$$

The values of b and c are so far unknown; they may be obtained by correlation with butadiene ($CH_2\cdot CH\cdot CH\cdot CH_2$). Here, if x_1, x_2 and x_3 are the lengths of the three C−C links

$$E(x_1x_2x_3)=(x_1-a)^2+(x_2-a)^2+(x_3-a)^2 +[2bx_1x_2+2c(x_1+x_2)]+[2bx_2x_3+2c(x_2+x_3)].$$

The first three terms are compression energies and the second two are interaction energies. The defining equations are

$$\begin{aligned} x_1-a+bx_2+c&=0\\ x_2-a+b(x_1+x_3)+2c&=0\\ x_3-a+bx_2+c&=0. \end{aligned}$$

If we put $x_1=x_3=1.347$A, $x_2=1.432$A, as predicted by the writer[1] from resonance calculations, we find that

$$b=0.400, \quad c=-0.590. \tag{4}$$

We can now use our general formulae to predict the lengths of the links in other molecules, both of chain and ring type. The reasonableness of our fundamental assumptions with regard to bond interaction will be verified by our ability to predict proper values for these other links; we shall find almost complete agreement between the lengths calculated according to the methods of this paper and of quantum-mechanical resonance.

Let us first apply our method to the allyl radical $CH_2\cdot CH\cdot CH_2$. It appears that the links are of equal length 1.372A, in excellent agreement with the value 1.366A predicted quantum-mechanically by the writer.[6]

Next let us consider the conjugated chain molecules $C_{2n}H_{2n+2}$; we find precisely the same general properties which have been found before; thus, if we number the links in order from one end, the odd links are all shorter than the even links, but both tend to the same limiting value, sufficiently far from the end. Table I shows the results thus obtained, and in Table II we show the predictions for the infinite conjugated chain; in this latter case it appears that the length of

TABLE II. *Lengths in the infinite conjugated chain.*

Link No.	1	2	3	4	5	6	7	Asymptotic Value
Length, resonance*	1.355	1.419	1.377	1.407	1.383	1.403	1.386	1.394
Length, present paper	1.354	1.414	1.384	1.399	1.391	1.395	1.393	1.395

* See reference 1.

[5] Terms in $x_1^2+x_2^2$ appear to be unnecessary; their presence is partly allowed for by the compression energy $(x_1-a)^2+(x_2-a)^2$.

[6] Coulson, Proc. Roy. Soc. **A164**, 383 (1938).

the jth link is given by the simple formula

$$x_j = 1.395 + 0.0805(-0.5)^j. \qquad (5)$$

The agreement is remarkably good; the differences nowhere exceed 0.008A.

When the calculations are applied to the ring compounds $C_{2n}H_{2n}$ $(n>1)$, it is found that all the links should have the length 1.395A. Quantum calculations, except for cyclobutadiene[1b] give lengths between 1.388 and 1.400A. Cyclobutadiene, however, is unstable, and Wheland[7] has shown that in this case the quantum calculations are liable to serious errors.

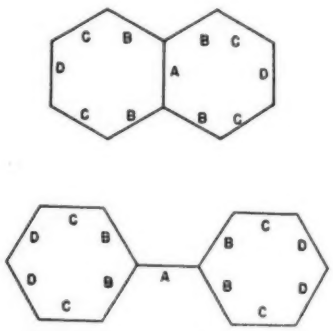

FIG. 1. The links of naphthalene and diphenyl.

Calculations have also been made for some more complicated structures, such as naphthalene and diphenyl. Using the notation of Fig. 1 the predicted lengths for the links are as shown in Table III; again there is excellent agreement. The lengths for naphthalene, using resonance methods are taken from a paper by the author shortly to be published, and those for diphenyl from some of the author's unpublished work. In the case of diphenyl, the difference between the two methods never exceeds 0.008A, and in particular the length of the interesting link A which connects the two closed rings, is almost the same in both treatments, being about halfway between a pure double and a pure single bond. In both molecules the relative order of the links is the same by both calculations, though there is a slightly more serious difference, amounting to about one-fortieth of an angstrom, in the lengths of the central link A in naphthalene.

[7] Wheland, Proc. Roy. Soc. **A164**, 397 (1938).

TABLE III. *Lengths of links in naphthalene and diphenyl.*

LINK		A	B	C	D	MEAN LENGTH
Naphthalene	resonance	1.418	1.410	1.378	1.401	1.397
	present paper	1.444	1.404	1.390	1.399	1.402
Diphenyl	resonance	1.449	1.397	1.387	1.389	1.396
	present paper	1.443	1.405	1.390	1.396	1.400

Similar calculations could be made for other molecules; but we do not make them because our object is chiefly to show, as the above tables have done, that lengths calculated in this way agree quite closely with those calculated on the basis of resonance; we could, also, with the inclusion of more parameters in Eqs. (1) and (2) have obtained even closer agreement between the methods. There is no point, however, in doing so at present, while it remains impossible to check the finer points of the bond lengths experimentally.

The empirical interaction term represented by Eq. (2) is one way of expressing the mutual influence of trigonal bonds; resonance is another way (in a sense artificial since it results from a forced separation of variables) of doing the same thing; before it can be used numerically, various unknown parameters have to be obtained by correlation with certain observed quantities. Our method is also empirical and again unknown parameters have to be obtained in the same way. Both treatments are essentially simplifications of the full quantum-mechanical analysis, which is evidently much too complicated to permit accurate calculations.

In conclusion we do not suggest that the present calculations should displace the resonance ones, since these latter are able to take account of other properties, such as excitation, fine structure, electrical and magnetic polarizabilities, etc., which our simple model is unable to include. But on the other hand, our calculations are very simple and provide excellent checks upon the other more laborious work.

Remarks on the Calculation of Bond Strengths

MILTON BURTON
Department of Chemistry, New York University, New York, New York

(Received July 23, 1939)

The hypothesis that predissociation as evidenced by sudden broadening of the rotation lines in an absorption spectrum may be used to establish the strength of the bond involved in the associated photochemical act is re-examined. It is shown to lead to incorrect conclusions in the few cases where its use seemed applicable. New values are derived for the C−C and C−H bond strengths in various compounds. The values are consistent among themselves and with observations in reaction kinetics but show a small spread due to secondary effects of adjacent double bonds. In free acetyl and formyl radicals the bonds are much weaker than in the stable compounds.

A HYPOTHESIS relating bond strength in polyatomic molecules and certain phenomena of predissociation has been used to calculate the strengths of C−C and C−H bonds in various molecules and free radicals.[1] Such calculations have been based essentially on the data indicated in Table I. It now appears that values so calculated are open to serious question.

FORMALDEHYDE

Only in the case of formaldehyde are the absorption data unambiguous. Of the rotation lines in the band at 2750A, one set is discrete and the other is diffuse. The diffuseness can be correlated with a bond strength only when we are certain of the associated photochemical act. Observations by Patat and Locker[2] on the effect of added oxygen in the photolysis of formaldehyde indicate that, while free hydrogen atoms are produced at <2700A, they are not formed at >2750A. Accordingly, $\lambda 2750$A was considered to correspond to the beginning of the reaction[1]

$$HCHO \xrightarrow{h\nu} H+HCO.$$

However, for $\lambda 2750$A to correspond exactly to the C−H bond strength, it must be assumed that it is a sufficiently complicated molecule so that the "predissociation hypothesis" applies. Gorin[3] states on the basis of his work on the photolysis of formaldehyde in the presence of iodine that reaction (1) takes place throughout the discrete region (although the evidence is not conclusive). Thus, it can be said definitely only that the corresponding 103.3 kcal.[1] is a maximum value for the strength of the C−H bond in HCHO. On the other hand, if the "predissociation hypothesis" is correct, it would be difficult to understand the formation of H atoms in the discrete region. If the hypothesis has any *practical* merit, it should be applicable in this case in order to make its use valuable, for the absorption spectrum of formaldehyde is one of the very few where a sudden broadening of a rotation line occurs without the simultaneous presence of a continuous background.

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begins at ~3100A[7] due to some contribution of energy from vibrational degrees of freedom[8] and that the beginning of diffuseness at ~3050A (at room temperature) reported by Henri[5] corresponds to the C−C bond strength.[1]

In this reasoning the existence of a continuum beginning at ~3400A was ignored. The continuum might, for example, be attributed to a one-step process

$$CH_3CHO+h\nu\rightarrow CH_4+CO, \qquad (3)^9$$

but an examination[9] of more recent evidence[10] indicates that free radicals are formed throughout the continuum. Indeed a calculation by Grahame[11] on the basis of that evidence indicates that the C−C bond strength in CH_3CHO may be as low as 75 kcal.

Furthermore, it has been pointed out by Noyes and by Leighton[12] that the density of the absorption spectrum may conceal the fact that the rotation line broadening actually begins at much shorter wave-lengths. Thus, if the "predissociation hypothesis" has merit, the C−C bond strength in CH_3CHO would be >93.1 kcal. whereas the work of Grahame clearly shows that it is less and probably as low as 75 kcal.

In this paper the value of 75 kcal. for B_{CC} (the C−C bond strength) in CH_3CHO is finally adopted because, as is shown elsewhere[13] it is the best value so far derived from reaction kinetics data. It may be compared with the value of 69.4 kcal. given by Rice and Johnston[14] on the basis of Paneth mirror experiments at ~1100°K.

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However, Noyes, Duncan and Manning,[16] who observed no bands shorter than 3027A in their work on acetone, reported that some of them had a really diffuse character. The assumption that diffuseness begins at 2945A was consequently unjustified.

In the case of acetone, as in that of acetaldehyde, the probable existence of a continuum[16] underlying the discrete region was neglected. By analogy with the case of acetaldehyde[9] it is here also possible that the continuum might correspond to the one-step process

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Let B_{CH} and B_{CC} be the C−H and C−C bond strengths in these compounds, respectively. The values for the heats of formation of methane and ethane are given[1, 17] as 346.5 and 575.7 kcal., respectively. Thus

$$B_{CC}=2B_{CH}-117.3 \text{ kcal.}$$

Assuming that the effects of substitution are approximately additive, Conant[18] has estimated

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B_{CC} in ethane to be 76.5 kcal. Kistiakowsky and Gershinowitz[19] have estimated from bond spectral data, that B_{CC} is 77 ± 4 kcal. in cyanogen. Grahame's calculation indicates a value for B_{CC} in CH_3CHO not greater than 75 kcal. The arbitrary assumption, that the effect of the adjacent double bond in acetaldehyde is such as to increase $B_{CC}\sim3$ kcal. over the normal (in ethane)[20] is justified in the consistency of the data. B_{CC} in ethane then is ~72 kcal. and B_{CH} in methane ~95 kcal. These values are to be compared with Pauling's calculated values of 82.5 and 100 kcal., respectively,[21] with a recent calculation[22] according to the method of Voge[23] which shows that a value of B_{CH} in methane $\backsimeq95$ kcal. is reasonable, and with the estimated value of B_{CH} in HCN = 94.5 kcal.[19]

Bond Strengths in Formaldehyde and Glyoxal

Let F_F be the heat of formation of gaseous formaldehyde from the gaseous atoms at 0°K and F_G be a similar value for glyoxal. Then for these compounds

$$B_{CC}=2B_{CH}+F_G-2F_F. \qquad 2$$

The value for F_F is given[1, 17] as 314.1 kcal. Using the data of Bichowsky and Rossini,[24] it may be shown[1, 17] that $F_G=541.1$ kcal. Thus

$$B_{CC}=2B_{CH}-87.1 \text{ kcal.}$$

In Table II there are given different values for B_{CC} depending on various assumed values for B_{CH} in formaldehyde. From the assumed values $B_{CC}\backsimeq72$ and 75 kcal. in C_2H_6 and CH_3CHO, respectively, it follows that B_{CH} in HCHO is ~85 kcal. and that B_{CC} in glyoxal is, consequently, ~83 kcal. The value $B_{CH}\backsimeq78$ kcal., assumed by Gorin,[10] leads directly to the extraordinarily low value $B_{CC}\backsimeq69$ kcal. Between the two choices the former should be favored, for ordinary organic theory would indicate a semi-double bonded character for C−C in the conjugated glyoxal system. On the other hand were we to accept the 103.3 kcal. value for B_{CH} we would run into trouble with B_{CH} in methane, for the latter (assuming the value of $B_{CC}\backsimeq75$ kcal. in CH_3CHO) would then be ~77 kcal. Similarly, B_{CC} in ethane would have the impossibly low value of ~36 kcal.

It follows, then, if we accept the 75 kcal. value in CH_3CHO, that the "predissociation hypothesis" does not apply even in the relatively simple and straightforward case of formaldehyde.

The Formyl C−H Bond in Acetaldehyde

By analogy to the choice of ~72 kcal. for B_{CC} in ethane it is assumed that, since the adjacent double bond in acetone has to divide its effectiveness between C−C links, B_{CC} in acetone is ~73.5 kcal. Taking the heats of formation of acetaldehyde and acetone as 555.6 and 790 kcal.,[1, 17] respectively, B_{CH} in the −CHO group of acetaldehyde then is ~91 kcal. This value, it may be seen, is intermediate between those of B_{CH} in formaldehyde and methane.

In considering the mechanism of the pyrolysis of acetaldehyde, it was shown that, since the bond-strength hypothesis required a value B_{CH} in the formyl group of ~115 kcal., a necessary intermediate step in the mechanism was the formation of CH_2CHO instead of CH_3CO.[25] Von Elbe[26] objected to such a conclusion because of the resultant difficulty in explaining the formation of peracetic acid in the photochemical oxidation of acetaldehyde.[27] The value $B_{CH}\backsimeq91$ kcal. in the formyl group of acetaldehyde resolves the difficulty for the formation of CH_3CO in the

Table II. *Various calculated values of the* C−C *bond strength in glyoxal.*

B_{CH} in HCHO, kcal.	B_{CC} in $(HCO)_2$, kcal.	Ref.
103.3	119.5	2
78	69	10
85	83	—

[19] G. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. **1**, 432 (1933).
[20] Cf. Gorin, Walter and Eyring, J. Am. Chem. Soc. **61**, 1876 (1939).
[21] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).
[22] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 572 (1939).
[23] H. H. Voge, J. Chem. Phys. **4**, 581 (1936).
[24] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corp., New York, 1936).
[25] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 675 (1939).
[26] G. von Elbe, J. Chem. Phys. **7**, 680 (1939).
[27] Cf. G. von Elbe and B. Lewis, J. Chem. Phys. **7**, 710 (1939).

chain by the reaction

$$CH_3+CH_3CHO \rightarrow CH_4+CH_3CO \qquad (6)$$

is then a likely process. Reaction (6) is ~4 kcal. exothermal and may be shown to have an energy of activation of ~16.9 kcal.[13]

Conclusion

In Table III there are summarized the most consistent values adduced in this paper for the strength of the C−C and C−H bond. It may be seen that, except for the free radicals, the spread of values is now much less than those calculated on the basis of the "predissociation hypothesis."[1] Furthermore the values are consistent with the requirements of the acetaldehyde decomposition mechanism.

Table III. *Some approximate* C−C *and* C−H *bond strengths.*

Bond	Compound or Free Radical	Bond Strength
C−C	C_2H_6	72
	$(CH_3)_2CO$	73.5
	CH_3CHO	75
	$(CHO)_2$	83
	CH_3CO	4
C−H	CH_4	95
	HCHO	85
	O CH_3C-H	91
	HCO	19

The bond-strength hypothesis has been shown not to have value for the computation of bond strengths even in the relatively clear-cut case of formaldehyde.

DECEMBER, 1939 JOURNAL OF CHEMICAL PHYSICS VOLUME 7

The Potential Energy Relationships in Normal and Excited Acetaldehyde[1]

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(Received July 23, 1939)

By a simple modification and extension of the system of potential energy hypersurfaces used to correlate the observations in the thermal and the photochemical decomposition of acetaldehyde it is shown that the following effects are explained: (1) the dependence on temperature and wave-length of relative probabilities of free-radical and ultimate molecule production in the primary photochemical act; (2) the disappearance of fluorescence at shorter wave-lengths or at higher temperatures; (3) the separate maxima for band and continuous absorption; (4) the high quantum yield reported at 3340A.

In a recent publication it has been shown that the behavior of acetaldehyde in thermal decomposition can be explained on the basis of a relatively simple group of potential energy hypersurfaces.[2] It was there assumed that the strength of the C−C bond in CH_3CHO is 93.1 kcal. but it was also pointed out that such an assumption was not necessary to the argument but was adopted principally as a matter of convenience. Since that time it has become increasingly evident that this assumption is incorrect and that a lower figure, ~75 kcal., is nearer to the truth.[3] The modification of the potential energy hypersurfaces in accord with this conclusion, as shown in Fig. 1, is without effect on the interpretation of thermal phenomena. However, it has some serious consequences in the interpretation of photochemical phenomena and aids considerably in the clarification and explanation of a number of diverse observations.

[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Boston, September 11, 1939.

[2] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 414 (1939). The reader is referred to this paper for a description and designation of the hypersurfaces. The same designation will be retained here.

[3] (*a*) D. C. Grahame, Paper presented before the Wisconsin Symposium, June, 1939. (*b*) Cf. Burton, Taylor and Davis, J. Chem. Phys. **7**, 1080 (1939). (*c*) M. Burton, *ibid.*, **7**, 1072 (1939).

The Potential Energy System

To begin with, it may be seen from Fig. 1 (representing in a rough way two-dimensional cross sections of the hypersurfaces involved) that the hypersurface **B**, for the potential energy of CH_3+HCO in a particular system of configurations, must now be drawn as repulsive instead of weakly attractive. This introduces a profound change into our conception of these hypersurfaces. Evidence has been introduced to show that in polyatomic molecules the onset of predissociation, of a type indicated by a sudden broadening of the rotation lines, probably occurs at an energy input which corresponds rather closely to the strength of the bond involved in the associated chemical act.[4] Subsequently, the assumption of an exact correspondence was made based on the idea that since the hypersurfaces involved are extremely complicated there is a high probability that an intersection and a transition should occur at an energy level corresponding *precisely* to the bond strength involved.[5]

As we must conclude that the condition just described cannot be true in the case of acetaldehyde, we can retain only a single part of the original concept; i.e., the region of onset of diffuseness corresponds to a crossing of the hypersurfaces involved. There is not an indefinite energy range for crossing of the hypersurfaces but the crossing is fairly well localized over a brief range, in this case in the approximate neighborhood of 93 kcal. above the ground state of the normal molecule. An alternative hypothesis would be that the crossing extends over an indefinite range but that hypersurface **B** is weakly attractive with a potential energy hump near 93 kcal. It will appear from the following discussion that excitation may take place directly to hypersurface **B** and that such excitation is associated with a continuum over the entire range involved, not merely over a range beginning at 93 kcal. The second hypothesis can therefore be discarded.

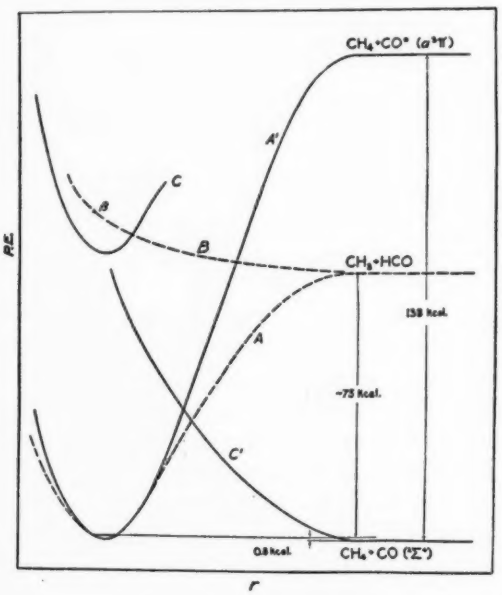

Fig. 1. Schematic representation of potential energy relationships in acetaldehyde.

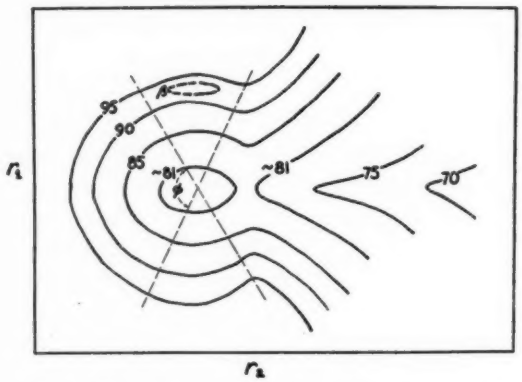

Fig. 2. Schematic representation of hypersurface **C**.

Absorption Spectrum

The discrete region

The discrete absorption region of acetaldehyde begins at ~3484A, corresponding to ~81.5 kcal.[6] According to the model we use, this band absorption is associated with excitation from the hypersurface **A** (which includes sections *A* and *A'*), describing the normal state of acetaldehyde, to the hypersurface **C**, which describes an excited state. Since at the longer wave-lengths the life of the excited state is long, fluorescence is strong and, with certain exceptions which will be noted later, molecular deactivation

[4] M. Burton and G. K. Rollefson, J. Chem. Phys. **6**, 416 (1938).

[5] M. Burton, J. Chem. Phys. **6**, 818 (1938); cf. *ibid.*, **7**, 682 (1939).

[6] P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

(or polymerization) is frequent and the quantum yield of the photochemical process is low.

At these longer wave-lengths, and corresponding to the discrete absorption, only one process is possible; namely, the slow rearrangement of the excited acetaldehyde, and its decomposition, into CH_4 and CO. The reactions may be written

$$CH_3CHO+h\nu\rightarrow CH_3CHO^*, \quad (1)$$

$$CH_3CHO^*\rightarrow CH_4+CO. \quad (2)$$

In a previous paper[2] it has been shown that reaction (2) may be explained in terms of an oscillation within the bowl of hypersurface **C**. One portion of this hypersurface is represented as a repulsive channel, shown as section C'. Reaction (2) occurs when in the course of its oscillation the molecule enters the repulsive channel C'; dissociation then takes place into CH_4 and CO. The yield of this reaction may be cut down by fluorescence, by molecular deactivation, or by polymerization.[7] The conditions in hypersurface **C** may be represented in a rough sort of way by a system of contour lines such as shown in Fig. 2. The line β represents the intersection (really a hyperline) between hypersurfaces **C** and **B**.

The diffuse region

Somewhere in the region near 3050A, depending on the temperature of the absorbing gas,[8] the absorption spectrum of acetaldehyde becomes diffuse. As has already been stated, this diffuseness may be attributed to a transition

$$\mathbf{C}\rightarrow\mathbf{B}, \quad (3)$$

which occurs when the excitation is to a level above β, the intersection of the two hypersurfaces. This transition is followed by the dissociation reaction

$$CH_3CHO^*\rightarrow CH_3+HCO. \quad (4)$$

The probability of the transition **C**→**B** is a function of the number of times the phase point representing the molecular configuration of acetaldehyde crosses the intersection and also of the time spent in the vicinity of the intersection during each crossing. The latter will be a maximum when the molecule is excited to an energy level in the energy range of the intersection. Factors which affect the former are discussed below.

The normal excitation of acetaldehyde (i.e., at low temperatures) is here represented as being to a point on hypersurface **C** such that a crossing of the intersection β does not occur during an early swing[9] even though the energy level of the excitation be sufficiently high. Thus at low temperatures there is a good probability that the molecule may dissociate via the repulsive channel C', reaction (2), or even lose its energy in one of the ways already mentioned, before transition (3) becomes possible. Such a state of affairs is represented in Fig. 2 as an excitation to a region of the hypersurface **C** within the angle ϕ.

The continuum

The whole absorption spectrum of acetaldehyde is underlaid by a continuum beginning at ~3400A and extending to shorter wave-lengths.[6] While the maximum of the band region occurs at ~3100A, the maximum of the continuum occurs close to 2750A.[6]

Rollefson and Grahame[10] have pointed out that this fact is best explained by the assumption that different upper electronic states are involved in the two different absorption acts. It is evident with the model here used that there are two possible absorption acts which would yield a continuum; i.e.,

$$\mathbf{A}+h\nu\rightarrow\mathbf{B}, \quad (5)$$

$$\mathbf{A}+h\nu\rightarrow C'. \quad (6)$$

Both **B** and the channel C' are repulsive and consequently dissociation would ensue within one vibration period and the spectrum would be continuous. The relative locations of the energy levels involved in the various hypersurfaces cannot well be represented in two- or three-dimensional diagrams. Nevertheless, it can be imagined that the hypersurfaces are so located that transition (5) occurs with high probability

[7] G. K. Rollefson, J. Phys. Chem. **41**, 259 (1937). Cf. M. Burton, *ibid.* **41**, 322 (1937).
[8] V. Henri, Trans. Faraday Soc. **25**, 765 (1929).
[9] For definition of a "swing" see G. K. Rollefson and M. Burton, J. Chem. Phys. **6**, 674 (1938).
[10] G. K. Rollefson and D. C. Grahame, J. Chem. Phys. **7**, 775 (1939).

at shorter wave-length; the maximum of the continuum is at 2750A. It will be seen that it conforms with the photochemical evidence to conceive of transition (6) as occurring with a low probability at long wave-lengths compared to the transition

$$\mathbf{A} \xrightarrow{h\nu} \mathbf{C}, \qquad (7)$$

which corresponds to reaction (1), the primary process associated with the band region. Further, we must assume that the relationship of the hypersurfaces is such that at wave-lengths around 3340A the probability of transition (6) exceeds that of (5); the absorption corresponding to (6) is assumed to have its maximum at longer wave-lengths than that corresponding to (5).

Photochemical Evidence

The effect of wave-length

The quantum yield of the photolysis of acetaldehyde increases with decrease of wave-length[6, 11] between 3130 and 2537A whilst at the same time the H_2/CO ratio in the product increases[11, 12] and the yield of polymer decreases.[11] It has been shown that such a result may be attributed to an increase in free radical production with decreasing wave-length.[7, 13] Rollefson and Grahame[10] have confirmed the effect of wave-length on the quantum yield at low temperature; they report values of $\gamma_{3132}=0.38$ at 23° and of $\gamma_{2652}=0.92$ at 21°C.

According to the model here presented, the absorption curves of Leighton and Blacet[6] indicate that at longer wave-length the transition $\mathbf{A} \xrightarrow{h\nu} \mathbf{C}$ is favored reaching its maximum probability at less than ~3100A. This transition does not lead to a high probability of dissociation since, on the average, the phase point of the molecule may have to execute a large number of swings before it can enter the channel C'. Crossing of the intersection β may also be an infrequent process. However, it must be remembered that such crossing and the accompanying transition **C→B** must be reckoned with even at wave-lengths exceeding 3050A (≏93.1 kcal.) since there is a possibility of an energy contribution from the available vibrational degrees of freedom.[14] There is thus a variation in the probability of the process **C→B** with wave-length and this variation is in a direction to agree with the observed increase of quantum yield with decrease of wave-length.

A more important factor relating quantum yield and wave-length, however, is the increased probability of the process $\mathbf{A} \xrightarrow{h\nu} \mathbf{B}$ at shorter wave-lengths. This absorption leads inevitably to decomposition and it may consequently be inferred that, under conditions where this transition occurs with *relatively* high probability, the quantum yield of the process is high. According to Leighton and Blacet,[6] the quantum yield γ_{3340} is 0.76 at ordinary temperature. This is to be compared with a value $\gamma_{3130}\backeq 0.2$ which they also report. They have called attention to the fact that the mercury line at 3342A falls directly between two band maxima, that the absorption of the line is principally due to the underlying continuum, and that a quantum yield larger than that for 3132A is consequently to be expected. According to Blacet and Volman[12] the H_2/CO ratio in the products at 3340A is 0.037, compared with 0.05 at 3130A. It seems, therefore, that the initial split is largely into ultimate molecules (i.e., by the mechanism $\mathbf{A} \xrightarrow{h\nu} C'$) and that the probability of transition (6) exceeds that of transition (5) at ~3340A.

We still have to account for two phenomena which are observed at ~3340A; namely, the fluorescence and the fact that the quantum yield is less than unity. Fluorescence is not to be expected when the excitation is to a state of short life; the explanation may be that the excitation is not strictly monochromatic for Leighton and Blacet[6] state that the absorption is *principally* due to the underlying continuum. The quantum yield would be reduced by the same process which produces fluorescence but part of the decrease at *all* wave-lengths (and particularly

[11] F. E. Blacet and J. G. Roof, J. Am. Chem. Soc. **58**, 278 (1936).

[12] F. E. Blacet and D. Volman, J. Am. Chem. Soc. **60**, 1243 (1938).

[13] On the other hand P. A. Leighton (Remarks at the Wisconsin Symposium, June, 1939) has obtained results, using a mirror method, which would indicate the total absence of free radicals at ~2537A. The results are somewhat anomalous for under the conditions of the experiment no gaseous product was observed.

[14] Cf. J. Franck and K. F. Herzfeld, J. Phys. Chem. **41**, 97 (1937).

at the shorter) is probably to be explained by a suggestion made originally by Leighton and Blacet[6] and more recently by Gorin,[15] namely that the quantum yield of the process involving free radicals is reduced by a back reaction

$$CH_3+HCO+M\rightarrow CH_3CHO+M. \quad (8)$$

Such a possibility must exist at low temperatures where the evidence is that HCO is stable[15, 16] and that the chains are extremely short.[17] The combination of radicals is generally held to end the chains;[6, 7, 12, 18] there does not seem to be any *a priori* reason why such a combination as (8) should be forbidden and indeed we are constrained to accept the view that at low temperatures the yield is reduced by this reaction.[18a]

Off-hand, it may seem that there is no need to assume the possibility of the transition $\mathbf{A} \xrightarrow{h\nu} C'$ at 3340A and that the low H_2/CO ratio can be adequately explained by the assumption of a longer chain length. Apart from the fact that extrapolation of high temperature quantum yields to low temperature[17] gives no evidence of chains sufficiently long to permit such an explanation, we would run into difficulty in an attempt to explain the short wave-length phenomena in the same way. The H_2/CO ratio at 2654A (and 30°C) is 0.126; at 2537A it is 0.155; at 2380A, 0.218.[12] Gorin [15] would ascribe the result to a greater efficiency of the reaction

$$HCO+CH_3CHO\rightarrow H_2+CO+CH_3CO, \quad (9)$$

when the HCO is formed with higher energy content and maintains that the observed effects can then be attributed to a falling-off in the primary free radical yield at shorter wave-lengths. This point of view, by itself, fails, however, to explain the sharp increase of quantum yield at 3340A. We adopt the other view that there are two different phenomena involved in continuous absorption, transitions (5) and (6), and that the latter has a maximum at longer wave-lengths and the former at shorter wave-lengths. Thus, the increase in the H_2/CO ratio runs nearly parallel to the increase in quantum yield[11] since the same process yields hydrogen and additional chains.

The effect of temperature

In consideration of a more naive model of potential energy hypersurfaces Rollefson and Burton[9] made the statement that, in general, the effect of increased temperature would be similar to that of decreased wave-length. On the other hand Rollefson and Grahame[10] have presented evidence that at 3130A the free radical process is 11.5 times as probable at temperatures above 200° as it is at room temperature. Leighton and Blacet[6] have found the quantum yields $\gamma_{3130}\backsimeq 0.2$; $\gamma_{3022}\backsimeq 0.28$; $\gamma_{2804}\backsimeq 0.5$. Blacet and Volman[12] show a smooth curve for the variation of H_2/CO ratio with wave-length in the entire range 3340–2380A. Thus, there is not the simple concordance between the effects of temperature and of wave-length which might be expected on the basis of the simpler model.

We have already indicated why it seems reasonable to localize the intersection β in a particular energy range. It will be seen that in Fig. 2 the intersection is so drawn that the phase-point of the excited molecule (assuming an excitation within the angle ϕ) has but a small tendency to cross the intersection during an early swing.[18b] We will now assume that the effect of increasing the temperature is so to shift the phase point of the molecule in the normal hypersurface that an excitation to the upper hypersurface in a region outside the angle ϕ becomes probable. Thus, the phase point of the molecule crosses β in an early swing and, since the transition **C→B** is assumed to be permitted, decomposition into free radicals ensues before either fluorescence, deactivation, or polymerization can occur. A simple rough calculation[3b] based upon the data of Rollefson and Grahame[10] and of Blacet and Volman[12] shows that the quantum yield of the primary process resulting in free radicals ${}_R\gamma_{3132}\backsimeq 0.32$ at high temperatures whereas ${}_R\gamma_{2652}\backsimeq 0.184$ at room temperature; if recombination is considered the values will be higher but their ratio will be approximately the

[15] E. Gorin, J. Chem. Phys. **7**, 256 (1939).
[16] M. Burton, J. Am. Chem. Soc. **60**, 212 (1938).
[17] J. A. Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934).
[18] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[18a] Reaction (8) is written as a three-body reaction simply because it seems more probable in that form. According to reference 3*b*, the bimolecular reaction between free radicals by which the chains are usually ended is not a simple combination.
[18b] In reference 9, this case is considered under *Class Ic*.

same. Thus, it is seen that more free radicals are actually produced per quantum absorbed via the indirect mechanism in the band region (**A**→**C**; **C**→**B**) than in an efficient part of the continuum. In the latter, part of the energy goes into the transition **A**→C' and the formation of ultimate molecules in the primary act. It seems that when the excitation is to a point on hypersurface **C** outside the angle ϕ there is practically no chance of dissociation through channel C' into the ultimate molecules.[18c] This is the condition at 3130A at high temperatures. Whatever ultimate molecules are primarily formed under those conditions probably result from the primary transition **A**→C'.

At shorter wave-lengths than 3130A, increased temperature would likewise serve to place the phase point of the molecule in the excited state **C** in a favorable position for an early crossing of the hyperline. Two factors operate, however, to reduce the resulting effect: (1) The phase point of the molecule spends a shorter time in the neighborhood of the crossing if the energy level be higher. The probability of the transition **C**→**B** is thus decreased. (2) At short wave-lengths the process **A**→**C** is not important. Most of the absorption is in the continuum and corresponds to transitions (5) and (6).

[18c] In reference 9, this case is considered under *Class Ia*.

Fluorescence

The model presented is in full accord with the observations. Fluorescence is limited to the band region;[6] i.e., to the region in which excited molecules of relatively long life are formed. From our point of view it makes little difference what the precise mechanism of the fluorescence may be. It may correspond to the process **C**→**A**+$h\nu$ or it may involve such steps as

$$CH_3CHO^* + (CH_3CO)_2 \rightarrow CH_3CHO + (CH_3CO)_2^*, \quad (10)$$

$$(CH_3CO)_2^* \rightarrow (CH_3CO)_2 + h\nu. \quad (11)[19]$$

Under either circumstance a relatively long life is required for the excited state of acetaldehyde in order that fluorescence may occur. At higher temperature the life of the excited state is decreased (the transition **C**→**B** becomes more probable) and the amount of fluorescence actually decreases with the temperature.

Similarly, at short wave-lengths ($\leq$2654A) the absorption is confined to the continuum and the life of the excited state is correspondingly short. Thus, if excited CH_3CHO is essential to the mechanism, fluorescence is unlikely under such conditions.

[19] Cf. M. S. Matheson and W. A. Noyes, Jr., J. Am. Chem. Soc. **60**, 1857 (1938).

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Chain Length and Chain-Ending Processes in Acetaldehyde Decomposition[1]

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(Received July 23, 1939)

The C−C bond strength in acetaldehyde is probably less than a previously postulated value of 93 kcal. and may be as low as the 75 kcal. value calculated by Grahame. The chain-ending processes in the pyrolysis, in the azomethane-induced decomposition, and in the photolysis of acetaldehyde are all bimolecular but it is clear that the processes in the second and the third decompositions cannot be identical. The uncertainty of the process in the pyrolysis introduces an uncertainty into Grahame's calculation. In any event, the process is not the combination of methyl radicals in the gas phase to yield ethane. In the photolysis (and perhaps in the pyrolysis) HCO seems to be involved in the chain-ending reaction. In the induced decomposition CH_3CO seems to be concerned. The recombination of methyl radicals as a wall reaction may occur in packed vessels. Activation energies of the various reactions are discussed.

[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of American Chemical Society, Boston, September 11, 1939.

IN a previous paper one of us[2] has considered the possibility that the beginning of diffuseness in the band absorption spectrum of acetaldehyde corresponds to the strength of the C−C bond in that compound. Since the diffuseness begins at ~3050A, it would follow that the strength of the C−C bond is ~93 kcal. Following the mechanism of Rice and Herzfeld[3] we have as the rate-controlling steps in the thermal decomposition the reactions

$$CH_3CHO \rightarrow CH_3 + HCO, \quad (1)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO, \quad (5)$$

$$CH_3CO(+M) \rightarrow CH_3 + CO(+M), \quad (4)$$

$$2CH_3 \rightarrow C_2H_6. \quad (6)$$

It follows that the over-all reaction is $\frac{3}{2}$ order and that the energy of activation is

$$E_i = E_5 + \tfrac{1}{2}(E_1 - E_6). \quad (i)$$

It has been shown that the thermal decomposition is not exclusively of the $\frac{3}{2}$ order but that there is a concomitant bimolecular reaction.[4] However, Letort[5] has succeeded in considering only that portion of the decomposition which is of $\frac{3}{2}$ order and has concluded that it has an energy of activation of 45.7 kcal.

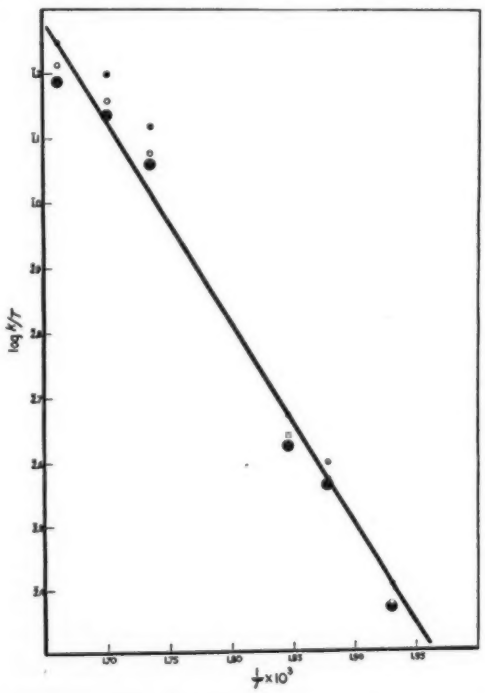

FIG. 1. Relative chain lengths in acetaldehyde decomposition induced by azomethane.
• $\alpha=0.30$; ○ $\alpha=0.67$; ● $\alpha=1.$

[2] M. Burton, J. Chem. Phys. **6**, 818 (1938).
[3] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

THE C−C BOND STRENGTH

Grahame[6] has drawn attention to the fact that data on the effect of temperature on the quantum yield of the photolysis of acetaldehyde[7] may be interpreted to indicate that $E_5 - \frac{1}{2}E_6 \simeq 8.3$ kcal. Substituting in Eq. (*i*) this yields a value of $E_1 \simeq 74.8$ kcal., setting an upper limit to the C−C bond strength, considerably below the 93 kcal. value previously suggested.

There is another way to test the 93 kcal. value which appears to be unambiguous in the sense that the experiments concerned seem to measure directly the reaction between acetaldehyde molecules and free CH_3 radicals. Allen and Sickman[8] have studied the decomposition of acetaldehyde induced by azomethane over a range of temperatures near 300°. They have calculated rate constants on the assumption that the first step in the chain is

$$CH_3NNCH_3 \rightarrow 2CH_3 + N_2, \quad (0)$$

instead of reaction (1) and come to a rate law of the form

$$\left(\frac{dP}{dt}\right)_0 = k_5 P_{Ac}\left[\frac{k_0 P_{Az}}{k_6}\right]^{\frac{1}{2}} = K_I \cdot (CH_3CHO)(k_0 P_{Az})^{\frac{1}{2}}, \quad (I)$$

where $(dP/dt)_0$ may with sufficient accuracy be taken equal to the total pressure change and P_{Ac} and P_{Az} are the partial pressures of acetaldehyde and azomethane, respectively. The energy equation then is

$$E_{ii} = E_5 + \tfrac{1}{2}(E_0 - E_6). \quad (ii)$$

From Eq. (*i*) it follows that, if E_1 is 93 kcal., $E_5 - \frac{1}{2}E_6 = -0.8$ kcal. A cursory examination of

[4] Cf. H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 414 (1939).
[5] M. Letort, Comptes rendus **199**, 1617 (1934).
[6] D. C. Grahame, Paper presented before the Wisconsin Symposium, June 22, 1939.
[7] G. K. Rollefson and D. C. Grahame, J. Chem. Phys. **7**, 775 (1939).
[8] A. O. Allen and D. V. Sickman, J. Am. Chem. Soc. **56**, 2031 (1934).

Allen and Sickman's data would seem to indicate a decrease in chain length with increase in temperature, as might be expected from such a value. When comparison is made at equal rates of production of methyl radicals and equal concentrations of acetaldehyde a different result is obtained.

The value of K_I divided by the absolute temperature is directly proportional to the chain length. In performing the calculation we have thought it expedient to take into account the fact that acetaldehyde may function to keep up the unimolecular rate in the thermal decomposition of azomethane. We have made the calculation for different assumed values of α (the relative efficiency of acetaldehyde in azomethane activation);[9] namely, 0.3, 0.67 and 1.0. The values of k_0 at the different temperatures were taken from curves relating log k_0 to log P, where $P=P_{Az}+P_{Ac}$. The curves for different temperatures were constructed by calculation from those given by Rice and Sickman, assuming E_0 to be independent of pressure and of temperature. The average values of log K_I/T (where T is the absolute temperature) thus calculated are plotted against $1/T$ in Fig. 1. It may be seen that the chain length actually increases with temperature.

The value of $E_5-\frac{1}{2}E_6$ calculated from the slope of the straight line in Fig. 1 is 14 kcal., which may be compared with Grahame's value of 8.3 kcal. Incidentally, it may be mentioned that variation in the assumed value of α does not change our conclusion as to $E_5-\frac{1}{2}E_6$ and that in averaging the results we eliminated one point at 313.3°C which departed extremely from the value which might be expected.

It follows that it seems advisable to reject 93 kcal. as the Γ -C bond strength in acetaldehyde.[10] Tentatively, we will adopt Grahame's value of ~75 kcal.[11]

The Chain-Ending Process and the Chain Length

In a discussion of the acetaldehyde chain Taylor and Burton[12] considered the possibility that the chain-ending reaction is termolecular

$$2CH_3+M\rightarrow C_2H_6+M \qquad (6')$$

and made the point that if M is acetaldehyde the final reaction rate is not changed thereby. Through an inadvertance it was not pointed out that it is essential to such a conclusion that the primary step be bimolecular

$$CH_3CHO+M\rightarrow CH_3+HCO+M. \qquad (1')$$

Under such circumstance the Rice-Herzfeld rate law and Eq. (*i*) follow and it is not possible to distinguish between a mechanism involving 1, 6 and one involving 1′, 6′. It is particularly difficult to reach a forthright conclusion with this limited information because, as has already been indicated, the ultimate molecule mechanism is of the same form:[4]

$$CH_3CHO+M\rightarrow CH_4+CO+M.$$

There is in the latter case, perhaps, a theoretical requirement that it be of the type of an induced predissociation;[4] there is no such requirement for the free radical mechanism and reaction (1′) might consequently be suspect for that reason.

On the other hand, the fairly good fit of the data of Allen and Sickman[8] to the rate law (*I*) can occur only if the chain-ending reaction is bimolecular and involves only free radicals. Consequently, their work has been interpreted in support of reaction (6) in spite of the fact that calculations of Kimball[13] and of Kassel[14] indicate that an ethane molecule formed in this way should have a mean life $\leq 10^{-12}$ sec.

Should further calculation indicate that the life of C_2H_6 formed from CH_3 radicals in a two-body process is actually $\gg 10^{-12}$ sec., the problem would be complicated, not simplified, for, as will be shown below, the bimolecular chain-terminating step has an energy of activation of ~17 kcal. Unless evidence is produced that such a high activation energy is required for the approach of two CH_3 radicals, we must conclude either that the value of ~17 kcal. represents a breaking-down in the symmetry of approach of

[9] Cf. O. K. Rice and D. V. Sickman, J. Chem. Phys. **4**, 239 (1936).

[10] Cf. M. Burton, J. Chem. Phys. **7**, 1072 (1939).

[11] The weakness of Grahame's calculation lies in the necessary assumption that the chain-ending mechanism is the same at ~300° as it is at the higher temperatures (~475°C) at which the $\frac{3}{2}$-order rate constant was determined. This assumption requires independent justification.

[12] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 675 (1939).

[13] G. E. Kimball, J. Chem. Phys. **5**, 310 (1937). Cf. reference 12.

[14] L. S. Kassel, J. Chem. Phys. **5**, 922 (1937).

the CH_3 radicals[15] as the temperature is increased or that a combination of CH_3 radicals in a two-body process cannot be the chain-terminating step in the simple photolysis.

A solution to the dilemma has been indicated in another connection by Allen and Sickman,[8] by Leighton and Blacet,[16] and by Spence and Wild.[17] They propose other possible chain-ending mechanisms; namely

$$CH_3+HCO\rightarrow CH_4+CO, \qquad (6a)$$

$$HCO+HCO\rightarrow H_2+2CO, \qquad (6b)$$

$$CH_3+CH_3CO\rightarrow C_2H_6+CO. \qquad (6c)$$

Following a similar scheme we might also write

$$CH_3CO+CH_3CO\rightarrow C_2H_6+2CO, \qquad (6d)$$

$$HCO+CH_3CO\rightarrow CH_4+2CO. \qquad (6e)$$

Rice and Herzfeld[3] have indicated that CHO may enter into the chain by the steps

$$HCO(+M)\rightarrow H+CO(+M), \qquad (2)$$

$$H+CH_3CHO\rightarrow H_2+CH_3CO \qquad (3)$$

and Blacet and Volman[18] have considered the possibility of the reaction

$$HCO+CH_3CHO\rightarrow H_2+CO+CH_3CO. \qquad (2')$$

The free acetyl radical, CH_3CO, is quite unstable above 60°C[17] while the free formyl radical, HCO, is still stable at 100°C[19] although it probably decomposes at somewhat higher temperatures.[6] Consequently, we might infer that reaction (6*b*) is unimportant as compared with (6*a*) at the higher temperatures and that reactions (6*c*), (6*d*) and (6*e*) can be neglected at all except the lowest temperatures.

It follows that if this scheme for ending the chains by a suitable bimolecular reaction is correct, the yield of ethane in either the photolysis or the pyrolysis of acetaldehyde should be a maximum at lower temperatures. The fact that no ethane has been found in the photolysis,[18] even at low temperatures, may be taken to indicate that CH_3CO is readily decomposed by other radicals acting as second bodies in a reaction of type (4), although this seems unlikely in view of the reported formation of diacetyl from free CH_3CO radical.[17, 20] On the other hand, it may be simply that reactions such as (6*c*), (6*d*) and (6*e*) are prevented on steric grounds. From the principle of microscopic reversibility it would be expected that reactions involving three products are less probable than those involving only two of the same general type. As for the relative probability of reactions (6*a*) and (6*c*) we are already constrained to believe that a free radical does not readily act to break a C—C bond[21] and that (6*c*) is unlikely. If we adopt this point of view we are compelled to conclude, as Blacet and Volman[18] indicate, that all the H_2 formed in the photolysis of acetaldehyde at low temperatures comes from reaction (2′).

It is now evident that there is no *a priori* reason for an assumption that the chain-ending mechanism is the same at all temperatures. Instead, we might expect a profound change in the chain-ending mechanism at temperatures at which the free formyl radical is unstable. Furthermore, since the HCO radical may be assumed to decrease in stability with increase in temperature, there should be fewer HCO radicals available at higher temperature so that the rate of the chain-ending reaction would not rise as rapidly as would accord with E_{6a} or, if the latter were zero, might actually fall off. The result would be to give a high value for $E_6-\frac{1}{2}E_{6a}$, as calculated for example from the work of Rollefson and Grahame.[7] If, however, E were determined under conditions where (6*a*) is the chain-ending reaction, the same effect would enter into the determination of E and $E_5-\frac{1}{2}E_{6a}$ and the calculation of the value of E_1 would be unaffected. It would have to be shown then, if we are to accept a value of E_1 calculated in this way, that the chain-ending reaction is the same in the temperature region in which the $\frac{3}{2}$-order reaction is studied and in the region in which $E_5-\frac{1}{2}E_6$ is determined.

[15] Kimball's calculation assumes symmetrical approach of the CH_3 radicals. Asymmetrical approach would permit asymmetrical oscillations and thus increase the life of the molecule.

[16] P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933). See J. A. Leermakers, *ibid.* **56**, 1537 (1934).

[17] R. Spence and W. Wild, J. Chem. Soc. 352 (1937).

[18] F. E. Blacet and D. Volman, J. Am. Chem. Soc. **60**, 1243 (1938).

[19] M. Burton, J. Am. Chem. Soc. **60**, 212 (1938).

[20] M. S. Matheson and W. A. Noyes, Jr., J. Am. Chem. Soc. **60**, 1857 (1938).

[21] Cf. F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (The Johns Hopkins Press, Baltimore, Md. 1933), p. 69.

That such an assumption cannot be made in any off-hand way is shown rather clearly by the results of Seddon and Travers[22] on the pyrolysis of acetaldehyde, who found no H_2 at 400° and a very small amount at 500°C. No ethane was found in the whole range 350–500° although propylene was found throughout.

It is now seen that the value $E_5-\frac{1}{2}E_6=14$ kcal. calculated from the data of Allen and Sickman is not directly comparable with the calculation of $E_5-\frac{1}{2}E_6=8.3$ kcal. made according to Grahame. If we are to follow the mechanism here delineated, the chain carriers in the first case can only be methyl radicals and the unstable CH_3CO, whereas in the latter case the more stable HCO is also included. Thus, the chain-ending reactions must be different and it would be expected that the chains in the azomethane induced case would be much longer since the chain-ending process must be less frequent than in the photolytic reaction. Calculation of the chain lengths in the two reactions under analogous conditions (equal acetaldehyde concentration and equal rates of free radical production at 300°) gives 1.84×10^5 as the chain length in the induced reaction compared with 8.44×10^2 in the photochemical reaction.[23]

Unfortunately, it is not possible to draw any conclusions as to the nature of the chain-ending processes from such a calculation, except that the processes are different.[24] However, we may arrive at an interesting clue as to the nature of another chain-ending process from some other data of Allen and Sickman. Their results show that the activation energy of the reaction in a packed vessel is 2.9 kcal. greater than in the unpacked vessel. The rate is considerably slower in the packed vessel, indicating that we are here concerned with a wall reaction of low activation energy and that the reaction is of the type

$$R+R'+W\rightarrow RR'+W, \qquad (6f)$$

so that the rate law involving a bimolecular chain-ending reaction still applies. However, since it is known that the accommodation coefficient in the case of methyl radicals falls off with increase in temperature,[25] we might expect a similar effect in this case. The result would be a slight departure from a rate law involving a simple bimolecular combination and the effect should be noticed at low temperatures in a rate constant slightly lower than that required by the simple mechanism (6*f*). Such an effect is actually shown by Allen and Sickman.

One other conclusion may be drawn from the data of Allen and Sickman. If $E_5-\frac{1}{2}E_{6a}=8.3$ kcal., taken from the data of Rollefson and Grahame, and $E_5-\frac{1}{2}E_{6f}=14.0+2.9=16.9$ kcal. from Allen and Sickman, then $E_{6a}-E_{6f}=17.2$ kcal. If (6*f*) actually is the combination of methyl radicals on the walls it is not unreasonable to assume a value $E_{6f}=0$. Then $E_{6a}=17.2$ kcal. and $E_5=16.9$ kcal. for the chain-continuing reaction. The latter figure may be compared with Rice and Herzfeld's assumed value of 15 kcal.[3]

It has been shown above that under comparable conditions of concentration and rate of free radical production the chain length is $>10^2$ as long in the induced case as in the photochemical decomposition of acetaldehyde. This can be attributed only to a lower probability of the chain-terminating step in the induced case and appears inconsistent with the low activation energy of that step (i.e., $2\times2.9=5.8$ kcal., calculated on the assumption that $E_{6f}=0$). When we consider the fact that free CH_3 is the most numerous radical present, it follows that reaction (6) cannot be the chain-terminating step if 5.8 kcal. represents a *true* energy of activation. It may either represent a breaking-down in the symmetry of approach of the CH_3 radicals or indicate that reaction (6*c*) is involved.

If it be assumed nevertheless, that reaction (6) really is the chain-terminating step for which the value $E_6=5.8$ kcal. (not necessarily a potential barrier) has been calculated and that it is the

[22] R. V. Seddon and M. W. Travers, Proc. Roy. Soc. London, **A156**, 242 (1936).

[23] The chain length calculated for the induced reaction is much longer than the actual ones which can be computed directly from the data of Allen and Sickman. The values calculated here are for azomethane pressures very much lower than those actually used by them. It is necessary to make the computation on this basis in order to make comparison with the photochemical case, in which the free radical production is of necessity low. Cf. the Appendix.

[24] It should be emphasized that this paper indicates merely that a bimolecular combination of free radicals cannot be the chain-terminating step. The step is doubtlessly a two-body radical interaction but its precise nature is still open to determination. However, the evidence does indicate that the radical interactions are different in the photolysis and in the induced reaction and any suggested mechanism must take that fact into account.

[25] F. A. Paneth, W. Hofeditz and A. Wunsch, J. Chem. Soc. 372 (1935).

chain-terminating step in the pyrolysis, then it follows from Eq. (*i*) that $E_1=63.4$ kcal., an extremely improbably value for the C−C bond strength in acetaldehyde.

It is therefore concluded that reaction (6) cannot be the chain-terminating step in any case of acetaldehyde decomposition. It is suggested that reaction (6*a*) involving the relatively stable HCO is the chain-terminating step in both the photolysis and the pyrolysis. In the induced case reaction (6*c*) is suggested as the chain-ending step; CH_3 reacts readily with CH_3CO which, although unstable and present in relatively low concentration, is (it must be remembered) produced in every step of the chain.

The nonappearance of ethane among the products of the photolysis shows clearly that even the three-body formation of ethane is extremely unlikely as compared with a reaction (6*a*) which has an energy of activation of at least 17.2 kcal.

Appendix

The calculation of chain length in the photolysis of acetaldehyde is based on the observations of Blacet and Volman[18] of the H_2/CO ratio in the products of the photolysis of acetaldehyde. We have concluded, as did Blacet and Volman, that all the hydrogen is formed by reaction (2′). From their observations at 2654A, it seems that H_2/CO tends under their conditions toward a limiting value of 0.2. By this we mean that at low temperature the yield of H_2 seems to be cut down by some cause, perhaps the (three-body) combination of formyl radicals, whereas at higher temperature the ratio H_2/CO is reduced by the incidence of the chain. We have merely extrapolated the first part of their curve to where it seems to level off. Furthermore, we have not taken into account the fact that the primary yield of free radicals may be reduced by the (three-body) reversal of reaction (1).[26] The assumption then that 20 percent of the quantum yield at room temperature is due to a primary free radical split is admittedly rough but is adequate for our purpose.

Since the quantum yield at room temperature is 0.92,[7] the quantum yield of the free radical split $_R\gamma_{2652}=0.2\times0.92=0.184$, also at room temperature. In our calculation of a typical chain length for the photolysis at 2652A at 300°C we have assumed that $_R\gamma_{2652}$ is unchanged at that temperature. The justification for such an assumption is discussed elsewhere.[26]

In the calculation of chain length, both CH_3 and HCO are assumed to be chain starters.

[26] Cf. T. W. Davis and M. Burton, J. Chem. Phys. **7**, 1077 (1939).

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Internal Rotation and Dipole Moment in Succinonitrile

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A new heterodyne-beat apparatus has been employed to determine the dipole moment of acetonitrile from −60° to +60° and that of succinonitrile from −90° to +90° in solution. By assuming each half of the succinonitrile molecule to have the same moment as the acetonitrile molecule, the observed moments have been used to calculate the height of the potential barrier which restricts rotation around the carbon-carbon single bond in succinonitrile and thereby causes the moment of the molecule to increase with rising temperature. The value 1.2±0.5 kcal. thus obtained is in better agreement with the value 1.5 obtained from the calculation of the sum of the various potential energies existing between the two halves of the molecule than is warranted by the necessarily approximate nature of the calculation.

A NUMBER of papers previously published from this laboratory have dealt with the relation of internal rotation to the dipole moments of various molecules.[1–8] With increasing knowledge of intramolecular forces more pene-

[1] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 2115 (1931).
[2] C. P. Smyth and S. E. Kamerling, J. Am. Chem. Soc. **53**, 2988 (1931).
[3] C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr. J. Am. Chem. Soc. **53**, 4242 (1931).
[4] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **54**, 2261 (1932).
[5] C. P. Smyth and W. S. Walls, J. Chem. Phys. **1**, 200 (1933).
[6] A. E. Stearn and C. P. Smyth, J. Am. Chem. Soc. **56**, 1667 (1934).
[7] C. P. Smyth and K. B. McAlpine, J. Am. Chem. Soc. **57**, 979 (1935).
[8] J. Y. Beach and D. P. Stevenson, J. Chem. Phys. **6**, 635 (1938).

trating attempts have been made to calculate the various potential barriers which may hinder rotation around the bonds and so reduce the resultant moment of two or more rotating or oscillating dipoles below the value to be found if rotation were unhindered. The calculated potential barriers have been found to be of the right order of magnitude to account for the observed reductions of the moments below the values calculated for the case of free rotation and for the dependence of the moments upon temperature. The excellence of the quantitative agreement sometimes obtained between the observed and the calculated values of the moments must, however, be regarded as fortuitous in view of the uncertainty of our knowledge of some of the forces involved. Beach and Stevenson[8] have calculated the potential barriers from the dipole moments, obtaining approximately 4 kcal./mole for ethylene chloride, 5 for ethylene chlorobromide and 6 for ethylene bromide and have extrapolated Altar's potential curve[9] to obtain a value of 5 for ethylene chloride, while Lennard-Jones and Pike[10] obtained values from 2.0 to 3.2 taking into account the variation of group moments with rotation. Recent thermal measurements[11–13] have shown a potential barrier of about 3 kcal. in ethane and propane in contrast to the much smaller calculated[14] value 0.3, while the restricting potential reported for propylene is only about 0.6 to 0.8.[13] While the explanation of these discrepancies remains to be determined, it seems worth while to seek such information as to the potential energy barrier hindering rotation around the C−C bond as can be obtained from the dipole moment of ethylene cyanide.

Ethylene cyanide has the advantage over the ethylene halides for an investigation of this sort that its dipoles are much larger and more definitely localized. Its great disadvantage is its low vapor pressure, which makes necessary the use of solution measurements to determine the dipole moment over a considerable range of temperature. Because of the low solubility of the substance in heptane and the rather limited range of temperature within which benzene is liquid, the substance was run in toluene solutions. In order to observe the influence of the solvent upon the apparent moment of a cyanide, acetonitrile was run under similar conditions of measurement.

Apparatus

Refractive indices were measured with a Pulfrich refractometer. The constant temperature bath and the pycnometer used for the measurements were similar to those used in previous work in this laboratory.[15] The dielectric constant cell described in the same place was modified by the elimination of the inner glass cylinder, by the use of gold cylinders instead of platinum in the condenser and by the insertion of a bulb in the outlet tube of the cell slightly above the level of the tops of the condenser cylinders as a means of removing the gas bubbles which usually form between the plates when the liquid to be measured is raised above room temperature. After twenty minutes had been allowed for the attainment of temperature equilibrium in the cell, the liquid to be measured was drawn up into the bulb, which was kept about 2 cm below the surface of the bath, and allowed to flow slowly back into the condenser. The removal of bubbles by this procedure prevented the abnormal falling off of values often observed at higher temperatures and led to the attainment of results as reliable as those at room temperature.

The cell was calibrated by means of benzene, the dielectric constant of which was taken as 2.276 at 25°. The capacity of the empty cell measured at 30° intervals from −90° to +90° was found to increase slowly but uniformly, the total increase over the 180° interval being 1.2 percent. The capacity determined at each temperature was used in calculating the dielectric constants measured at that temperature. During all the dielectric constant measurements, the level of the toluene bath surrounding the cell was kept constant by siphoning the liquid into

[9] W. Altar, J. Chem. Phys. **3**, 460 (1935).
[10] J. E. Lennard-Jones and H. H. M. Pike, Trans. Faraday Soc. **30**, 830 (1934).
[11] G. B. Kistiakowsky and F. Nazmi, J. Chem. Phys. **6**, 18 (1938).
[12] G. B. Kistiakowsky, J. R. Lacher and Fred Stitt, J. Chem. Phys. **6**, 407 (1938).
[13] G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, J. Chem. Phys. **6**, 900 (1938).
[14] H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[15] C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. **50**, 1547 (1928).

an auxiliary reservoir. The fixed capacity of the cell decreased by 0.2 percent over the 180° temperature range because of decrease in the dielectric constant of the bath toluene with rising temperature.

The dielectric constants were measured with a newly constructed alternating-current-operated heterodyne beat apparatus similar to that described by Stranathan.[16] It consisted of an oscillator of frequency 520 kilocycles fixed by a quartz crystal beating against a Hartley oscillator, the frequency of which was controlled by a variable precision condenser in parallel with the cell to be measured. The beats between these two oscillators were matched against the note of a 1000-cycle tuning fork operated on 6 volts d.c. The beats reached a phone through a detector and amplifier circuit, while the power was supplied by a vacuum tube rectifying circuit operated by 110 volts a.c. The apparatus had a precision of setting far beyond the accuracy of the precision condenser employed, which, as the result of very careful calibration, was sufficient to give an accuracy of about 0.05 percent in the dielectric constant values. In an attempt to obtain greater precision in the capacity measurement, a 100$\mu\mu$f mica condenser was switched in series with the precision condenser in the manner commonly employed in gas measurements. The precision of setting thus obtained warranted calculation of the dielectric constant values to the fifth decimal place, but, although a consistent series of results was obtained for seven solutions of acetonitrile in heptane running from 0.00425 to 0.00007 mole fraction of acetonitrile, the series measurements sometimes showed differences as large as 0.0025 from the seemingly more dependable dielectric constant values obtained directly. These latter values are reported in Table I.

Purification of Materials

Benzene.—Benzene was purified in the usual manner[17] by shaking with concentrated sulfuric acid, washing, drying with calcium chloride, fractional crystallization, refluxing over sodium wire, and distillation; d_4^{25} 0.87344; n_D^{25} 1.49814.

Toluene.—Toluene was shaken with concentrated sulfuric acid, distilled, dried over sodium, and fractionated; b.p. 110.6–110.8°; d_4^{25} 0.86098; n_D^{15} 1.49968.

Acetonitrile.—Material from the Eastman Kodak Company was dried with calcium chloride, refluxed repeatedly over phosphorus pentoxide until no further coloration appeared, distilled into freshly fused potassium carbonate, distilled from it, and finally fractionated, ground glass joints being used throughout. The middle portion was retained for measurement; b.p. 81.77° (765.0 mm); d_4^{25} 0.77765; n_D^{25} 1.34172; n_D^{20} 1.34424; ϵ^{25} 32.0.

Succinonitrile.—Material from the Eastman Kodak Company was twice recrystallized from acetone and vacuum distilled four times at about 1 mm, boiling at about 108° at this pressure.

Experimental Results

The dielectric constants ϵ and the densities d of the solutions containing mole fraction c_2 of the cyanide in benzene or in toluene are given in Table I, together with the values of the polarization P_2 of the cyanides calculated by means of the equations

$$P_{12}=\frac{\epsilon-1}{\epsilon+2}\frac{(1-c_2)M_1+c_2M_2}{d}$$

and

$$P_2=\frac{P_{12}-P_1}{c_2}+P_1, \qquad (1)$$

in which P_{12} is the polarization of the solution, P_1 is that of the solvent, and M_1 and M_2 are the molecular weights of the solvent and solute, respectively. The values of P_2 are extrapolated to $c_2=0$ to obtain P_∞, from which the dipole moment μ is obtained as

$$\mu=0.0127\times10^{-18}((P_\infty-MR_D)T)^{\frac{1}{2}}, \qquad (2)$$

in which T is the absolute temperature and MR_D is the molar refraction for the D sodium line, obtained from the experimental data for acetonitrile and calculated for succinonitrile from the refraction of acetonitrile and the atomic refraction of hydrogen. The values of P_∞ and μ are given in Table II, the values of μ for acetonitrile

[16] J. D. Stranathan, Rev. Sci. Inst. **5**, 334 (1934).
[17] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **54**, 1854 (1932).

TABLE I. *Dielectric constants, densities and polarizations.*

BENZENE-ACETONITRILE AT 25°C

c_2	ϵ	d	P_2
0.00000	2.276	0.87344	(26.67 = P_1)
.00774	2.398	.87311	239.0
.02134	2.616	.87248	229.1
.03818	2.895	.87171	219.6
.04066	2.927	.87162	217.9
.20040	5.736	.86238	143.8

TOLUENE-ACETONITRILE

c_2 =	0.01302	0.02701	0.04775	0.07065
t, °C	ϵ			
−60	2.870	3.156	3.551	4.007
−30	2.753	2.994	3.329	3.727
0	2.644	2.852	3.150	3.459
30	2.547	2.730	2.988	3.271
60	2.451	2.613	2.831	3.085
	d			
−60	0.93911	0.93865	0.93808	0.93753
−30	.91174	.91125	.91061	.91004
0	.88400	.88344	.88272	.88216
30	.85600	.85538	.85468	.85395
60	.82700	.82645	.82546	.82472
	P_2			
−60	282	265	238	220
−30	260	245	222	207
0	245	231	212	194
30	233	220	203	187
60	220	209	192	181

TOLUENE-SUCCINONITRILE

c_2 =	0.00000	0.00732	0.01125	0.01849	0.02775	0.04396
t, °C	ϵ					
−90	2.688	2.850				
−60	2.605	2.756	2.842			
−30	2.524	2.664	2.743	2.881		
0	2.447	2.576	2.648	2.776	2.946	
30	2.372	2.490	2.555	2.673	2.827	3.093
60	2.299	2.405	2.465	2.573	2.711	2.952
90	2.226	2.321	2.373	2.471	2.593	2.811
	d					
−90	0.96733	0.96837				
−60	.93965	.94071	0.94125			
−30	.91203	.91307	.91361	0.91466		
0	.88438	.88541	.88593	.88701	0.88834	
30	.85639	.85743	.85796	.85903	.86035	0.86267
60	.82752	.82855	.82909	.83016	.83149	.83387
90	.79765	.79870	.79924	.80029	.80160	.80390
	P_1	P_2				
−90	34.27	304				
−60	34.14	301	300			
−30	34.03	294	296	287		
0	33.87	294	293	284	276	
30	33.73	288	286	279	272	259
60	33.61	278	276	273	265	253
90	33.48	268	269	264	256	247

at −90° and 90° being obtained by extrapolation of the values at the intervening temperatures.

DISCUSSION OF RESULTS

The considerable increase of the apparent value of the moment of acetonitrile with rising temperature shows the strong effect of solvent in lowering the moment. The apparent value at 30° in toluene solution is slightly lower than that found in benzene solution at 25° as would be expected from the lower dielectric constant of benzene. The fact that the rough value found in heptane, which has a lower dielectric constant than benzene, is slightly lower than that found in benzene is presumably due to error in the determination of the value in heptane. The empirical equation of Müller[18]

$$\mu_S/\mu_G = 1 - 0.038(\epsilon - 1)^2, \qquad (3)$$

[18] H. Müller, Physik. Zeits. **34**, 689 (1933).

TABLE II. *Polarizations at infinite dilution and dipole moments.*

	CH_3CN $MR_D = 11.1$		$C_2H_4(CN)_2$ $MR_D = 20.0$	
t, °C	P_∞	$\mu(\times 10^{18})$	P_∞	$\mu(\times 10^{18})$
	Solvent: C_7H_{16}			
25	(258)	(3.45)		
	Solvent: C_6H_6			
25	265	3.51		
	Solvent: $C_6H_5CH_3$			
−90		(3.10)	314	2.94
−60	305	3.18	311	3.16
−30	282	3.26	308	3.36
0	262	3.32	304	3.54
30	247	3.40	297	3.68
60	232	3.45	289	3.80
90		(3.50)	281	3.90

in which μ_S is the moment observed in solution, μ_G, the true moment determined in the vapor state, and ϵ, the dielectric constant of the solvent, when applied to the values of μ_S for acetonitrile in Table II, gives calculated values of μ_G lower than the value 3.94 observed for the gas[19] and varying with the temperature. Approximate doubling of the empirical factor, 0.038 to 0.075, leads to a calculated value 3.94 for μ_G which is independent of temperature.

It is evident that the magnitude of the solvent effect renders impossible a very precise interpretation of the variation of the moment of succinonitrile with temperature. It should, however, be possible to set a limit to the value of the potential energy between the two halves, $-CH_2CN$, of the molecule which restricts the rotation around the C−C bond and gives rise to increase of moment as increasing kinetic energy resulting from rise of temperature tends to overcome the restriction. That such increase of moment occurs is evident not only in the apparent values of the moments in Table II, which rise more than twice as much for succinonitrile as for acetonitrile, but also in the much slower rate of decrease of the polarization of succinonitrile with rising temperature. The simplest procedure would be to assume that the effect of solvent upon the $C_2H_4(CN)_2$ molecule is the same as that upon the CH_3CN molecule and apply a modified form of the Müller equation

$$\mu_S/\mu_G = 1 - 0.075(\epsilon - 1)^2$$

to the values of μ_S for succinonitrile in Table II. The values of μ_G thus obtained increase from 3.74 at −90° to 4.39 at 90° as compared to the value 5.23 which the molecule should have if each half had the same constant moment 3.94 as CH_3CN and could rotate freely around the C−C bond. An objection to this procedure is that it fails to take account of the effect of the solvent in diminishing the variation of the mutual potential energy of the two halves of the molecule with rotation around the C−C bond. In the case of the ethylene halides, this effect has been found[6] to increase the moment to such an extent that it is higher in solution than in the vapor state. In spite of these difficulties, the magnitude of the variation in potential energy between the two halves of the molecule may be obtained from the observed moments and compared with the energy calculated from theoretical considerations. For a molecule containing two dipoles of moments m_1 and m_2 able to rotate more or less about a common axis, an expression for the moment μ may be written as follows:

$$\mu^2 = m_1^2 + m_2^2 - 2m_1m_2 \cos\theta_1 \cos\theta_2 + \frac{2m_1m_2 \sin\theta_1 \sin\theta_2 \int_0^\pi \cos\varphi \exp(-V(\varphi)/RT)d\varphi}{\int_0^\pi \exp(-V(\varphi)/RT)d\varphi} \quad (4)$$

where $V(\varphi)$ is the potential function of φ, the angle between the projections of m_1 and m_2 upon the plane perpendicular to the axis of rotation and θ_1 and θ_2 are the angles made by the common axis of rotation and the directions of the moments m_1 and m_2, respectively. The evaluation of such a potential function has been the theme of various papers.[3, 8–10, 20, 21] It is the purpose of the present discussion to consider $V(\varphi)$ for the succinonitrile molecule.

Equation (4) may be rearranged to become

$$\frac{\mu^2 - m_1^2 - m_2^2 + 2m_1m_2 \cos\theta_1 \cos\theta_2}{2m_1m_2 \sin\theta_1 \sin\theta_2} = \frac{\int_0^\pi \cos\varphi \exp(-V(\varphi)/RT)d\varphi}{\int_0^\pi \exp(-V(\varphi)/RT)d\varphi}. \quad (5)$$

For molecules with identical dipoles, $m_1 = m_2 = m$, and identical angles, $\theta_1 = \theta_2 = \theta$, like succinonitrile, the equation reduces to

$$\frac{\mu^2}{2m^2 \sin^2\theta} = 1 + \frac{\int_0^\pi \cos\varphi \exp(-V(\varphi)/RT)d\varphi}{\int_0^\pi \exp(-V(\varphi)/RT)d\varphi}. \quad (6)$$

[19] L. G. Groves and S. Sugden, J. Chem. Soc. 158 (1937).

[20] L. Meyer, Zeits. f. physik. Chemie **B8**, 27 (1930).

[21] J. M. Sturtevant, J. Am. Chem. Soc. **55**, 4478 (1933).

The ratio of the integrals is the same whether integration is carried over π or 2π. When $V(\varphi)=0$, it takes the form of the common equation for complete freedom of rotation,

$$\mu=\sqrt{2}m \sin \theta. \quad (7)$$

$V(\varphi)$ may be evaluated by considering the various types of forces between cyanide groups. Steric hindrance in which freedom of rotation is prevented because of actual collision of the rotating groups does not occur here. Steric repulsions, arising from the interchange energy of atoms which are not bound are obtained by use of the Morse equation.[22] London or van der Waals forces are calculated. Two effects are caused by the large permanent electric moments of the cyanide groups: the one, direct interaction of dipoles, leads to repulsion; the other involves the attractive forces caused by the inductive effect of a dipole upon a polarizable group.

If the total bonding energy of the two cyanide groups consists of 20 percent Coulombic and 80 percent interchange energy, application of the perturbation theory leads to an energy of steric repulsion equal to 20 percent of the total bonding energy.[23, 24]

To obtain the total bonding energy recourse is had to the Morse equation,[22]

$$E=D'[\exp\{-2a(r-r_0)\} - 2\exp\{-a(r-r_0)\}]. \quad (8)$$

D', expressed in kcal., is the sum of the spectroscopic energy of dissociation and the zero point energy, $D'=D+1/2h\omega_0=D+\omega_0/(2\times 352)$, where the frequency ω_0 is expressed in wave numbers.

$$a=0.1227\omega_0\frac{m_1m_2}{352D'(m_1+m_2)};$$

in which m_1 and m_2 are the masses of the atoms in question. r is the distance associated with a particular value of E; r_0 is the distance at the maximum value of D'. The quantities, D, ω_0, and r_0, necessary for the evaluation of E, are given by Sponer.[25]

[22] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[23] J. C. Slater, Phys. Rev. **38**, 1109 (1931).
[24] H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[25] H. Sponer, *Molekülspectren* (J. Springer, Berlin, 1936).

The carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen distances of the cyanide groups as a function of the angle of rotation were obtained by use of a model similar to that employed by Smyth, Dornte and Wilson[3] and the covalent bond distances 1.54A for C−C and 1.16 for C≡N. The total energies were calculated for triply bound carbons, nitrogens, and carbon-nitrogen at their respective distances. Accounting for the carbon to nitrogen energy twice, the energies were summed. Twenty percent of this sum was used as the steric repulsion given as U_S in Table III in kcal. as a function of the angle of rotation φ. The energy U_d of van der Waals attraction, or London forces, may be calculated by the simple dispersion effect formula,[26]

$$U_d=-3/4h\nu_0\alpha^2/r^6, \quad (9)$$

in which, h is Planck's constant, ν_0 the "proper" frequency, α the polarizability of the cyanide group, and r the distance between the centers of the nitrogen-carbon bonds in the cyanide groups. The $h\nu_0$ was taken as the average of the first ionization potentials of carbon and nitrogen, 11.217 and 14.38 volts, respectively. The polarizability of the cyanide group was approximated as 3.6×10^{-24} cc.

The energy of attraction U_i due to the inductive action of a permanent electric moment

TABLE III. *Calculated energies of attraction and repulsion (kcal./mole).*

$\varphi°$	U_S	U_d	U_i	U_m	U
0	3.45	−3.18	−1.65	6.95	5.57
10	3.36	−3.06	−1.59	6.81	5.52
20	3.06	−2.73	−1.41	6.44	5.36
30	2.55	−2.28	−1.18	5.97	5.06
40	2.09	−1.79	−0.93	5.38	4.75
50	1.60	−1.40	− .73	4.87	4.34
60	1.23	−1.05	− .55	4.38	4.01
70	0.89	−0.81	− .42	3.97	3.63
80	.69	− .61	− .32	3.58	3.34
90	.52	− .48	− .25	3.30	3.09
100	.41	− .37	− .20	3.04	2.88
110	.33	− .30	− .16	2.88	2.75
120	.27	− .25	− .13	2.72	2.61
130	.21	− .21	− .11	2.58	2.47
140	.17	− .18	− .10	2.49	2.38
150	.15	− .17	− .09	2.44	2.33
160	.14	− .16	− .08	2.39	2.29
170	.13	− .15	− .08	2.35	2.25
180	.13	− .15	− .08	2.34	2.24

[26] F. London, Trans. Faraday Soc. **33**, 8 (1937).

upon a polarizable group may be calculated from the formula[26]

$$U_i = -2\alpha\mu^2/r^6, \qquad (10)$$

where μ is the permanent electric moment of the cyanide group. The value of the moment used here and in the calculation of U_m was 3.44. The potential energy U_m between the two dipole moments as a function of the angle of rotation φ was calculated by the method of Smyth, Dornte and Wilson.[3]

The energies, U_S, due to steric repulsion, U_d, due to van der Waals attraction, U_i, due to dipole induction, U_m, due to dipole-dipole repulsion, and $U = U_S + U_d + U_i + U_m$, expressed in kcal. per mole are tabulated in Table III and plotted in Fig. 1 as functions of the angle φ.

These calculations neglect the effects of the two hydrogens in each half of the molecule, which, as previously stated, were calculated as giving a potential barrier of only 0.3 kcal. in ethane, while the potential barrier in ethane has been found experimentally to be about 3 kcal. The inclusion of the hydrogen-hydrogen and hydrogen-cyanide interactions would, of course, introduce additional maxima and minima in the curve given by the values in Table III and would somewhat alter the height of the single potential barrier of $5.57 - 2.24 = 3.33$ kcal., without, however, greatly changing its magnitude. In view of the uncertainties inherent in the calculations of the energies in Table III, it has not seemed worth while to make these additional calculations. Another factor neglected in obtaining the energy values in Table III is the lowering of each of the two cyanide dipole moments by the inductive action of the other. This calculation has been made by the method employed in an earlier paper.[27] It gives a lowering of the moment for $\varphi = 0°$ sufficient to reduce U_m from 6.95 to 4.95 and, for $\varphi = 180°$, sufficient to reduce U_m from 2.34 to 2.12. The total potential barrier is, thereby, reduced to $3.57 - 2.02 = 1.55$ kcal.

An empirical potential function may be obtained by setting

$$V(\varphi) = V_0(\cos\varphi + 1)/2, \qquad (11)$$

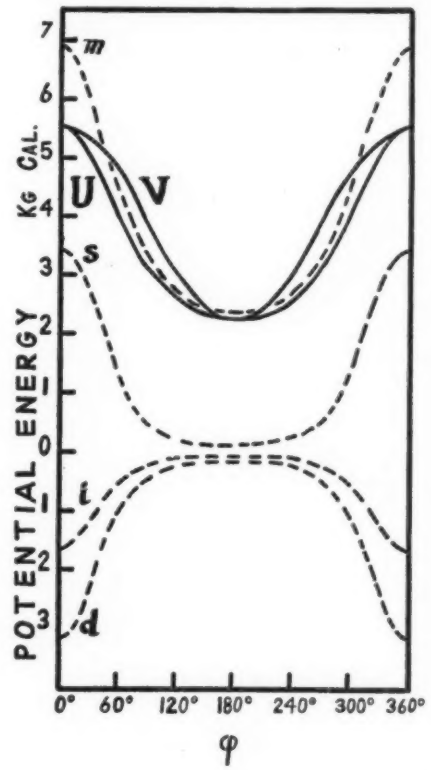

FIG. 1. Potential energies U_d, U_i, U_s, U_m, U and $V(\varphi)$ as functions of φ.

where V_0 is the potential barrier. $V(\varphi)$ is represented by the curve V in Fig. 1. In view of the lowering of the potential barrier to 1.55 calculated as the result of inductive effect, the value 3.33 given by the values of U in Table III may be regarded as an upper limit for the barrier. This upper limit may be tested by use in Eq. (6) in two different ways. $V(\varphi)$ may be set equal to U in Table III or to $3.33(\cos\varphi + 1)/2$ according to Eq. (11). These values of $V(\varphi)$ were substituted in Eq. (6) and the integrals were evaluated by a graphical method, although the methods employed by Beach and Stevenson[8] and Mizushima and Higasi[28] might have been employed. The values of the moment of acetonitrile in Table II uncorrected for solvent effect are used for m at each temperature T in Eq. (6) to obtain a calculated value of the moment. The values calculated in these two ways, together with those calculated on the assumption of complete freedom of

[27] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **1**, 190 (1939).

[28] S. Mizushima and K. Higasi, Proc. Imp. Acad. **8**, 482 (1932).

TABLE IV. *Calculated moments of succinonitrile* ($\times 10^{18}$).

t, °C	OBSERVED	$V(\varphi)=U$	$V(\varphi)=V_0(\cos\varphi+1)/2$	$V(\varphi)=0$
−90	2.94	1.89	1.27	4.12
−60	3.16	2.06	1.43	4.23
−30	3.36	2.26	1.61	4.24
0	3.54	2.38	1.83	4.42
30	3.68	2.53	2.01	4.51
60	3.80	2.68	2.17	4.58
90	3.90	2.82	2.31	4.65

rotation, that is, for $V(\varphi)=0$, by means of Eq. (7) are given in Table IV, which repeats the observed values for comparison. The values used for $V(\varphi)$ are given at the head of each column of calculated moments.

The increase with increasing temperature of the moment values calculated for $V(\varphi)=0$ is, of course, entirely due to the effect of solvent upon the apparent values of the moment of acetonitrile used in the calculation. A portion of the larger increase in the other calculated values and probably in the observed values also arises from this solvent effect. Both sets of values calculated on the basis of a potential barrier of 3.33 kcal. show about the same increase with temperature as the observed, but both are much too low, the values for $V(\varphi)=U$ being the better of the two sets. It is evident, therefore, that the potential barrier 3.33 kcal. tried as an upper limit is much too high and that the value 1.55 kcal. is, as would be expected, more nearly correct. Instead, however, of basing upon this lower potential barrier another set of calculations like those whose results form Table IV, the calculation is reversed and the observed values of μ and the value of m given by the moment of acetonitrile are substituted in Eq. (6) to calculate the ratio of the two integrals, from which values of $V(\varphi)$ are obtained graphically.

The relation of $V(\varphi)/RT$ to the ratio of the integrals $r(\varphi)$ is shown in Table V, the first column giving the values of the integral ratio,

$$r(\varphi)=\frac{\int_0^{\pi}\cos\varphi\exp\left(-V(\varphi)/RT\right)d\varphi}{\int_0^{\pi}\exp\left(-V(\varphi)/RT\right)d\varphi},$$

the second the values of $V(\varphi)/RT$ where $V(\varphi)=U$, and the third, the values when $V(\varphi)=V_0/2(\cos\varphi+1)$. Fig. 2 represents the values graphically.

Constancy of the value of the potential barrier V_0 obtained from $V(\varphi)$ should give evidence as to the correctness of the method. Values of V_0 obtained by using the calculated relation $V(\varphi)=U$ and the empirical relation $V(\varphi)=V_0(\cos\varphi+1)/2$ are given in Table VI. Under each of these two headings are given two columns of energy values, (a) obtained with $m=\mu_{CH_3CN}$, the uncorrected moment observed for acetonitrile at the temperature t, (b) obtained with $m=3.94$, the gas value for acetonitrile.

The values obtained by using $V(\varphi)=V_0/2\times(\cos\varphi+1)$ and $m=\mu_{CH_3CN}$ show a small but appreciable rise with rising temperature, while those in the other three columns show average deviations of only 2.5 percent from 1.15 kcal., 1 percent from 1.97, and 1 percent from 1.34, respectively.

The values obtained from the potential barrier would not be altered by solvent effect if the latter is the same for succinonitrile as for acetonitrile since the correction factors applied to μ and m in Eq. (6) would cancel out leaving the result already obtained. If the solvent has a loosening action, as appears to be the case with the ethylene halides, so that the solution values are higher than those that the vapor would have, the value 1.15 is somewhat low. As the value 3.94 represents an upper limit for m, the tendency is for the values of the potential barrier calculated with it to be high. Actually, the inductive action of the dipoles lowers the effective value of m particularly in the neighborhood of $\varphi=0$ and thus, as previously pointed out in connection with the values of U in Table III, lowers the potential barrier. It appears, therefore, that the energy values calculated with

TABLE V. *Relation of integral ratio to potential function.*

$-r(\varphi)$	U/RT	V_0/RT
0.1	0.52	0.36
.2	1.08	.74
.3	1.65	1.20
.4	2.32	1.66
.5	3.15	2.20
.6	4.22	2.90
.7	5.78	3.82
.8	9.25	5.44
.9	—	8.36
1.0	∞	∞

$m=3.94$ are somewhat high. The average of the three sets of constant potential barrier values in Table VI is 1.49 as compared to the value 1.55 kcal. previously calculated from the forces between the two cyanide groups, but the excellence of this agreement is fortuitous. It appears probable that the lower value 1.15 is more nearly correct and it is not unreasonable to assign a value 1.2 ± 0.5 kcal. to the potential barrier hindering internal rotation in ethylene cyanide,

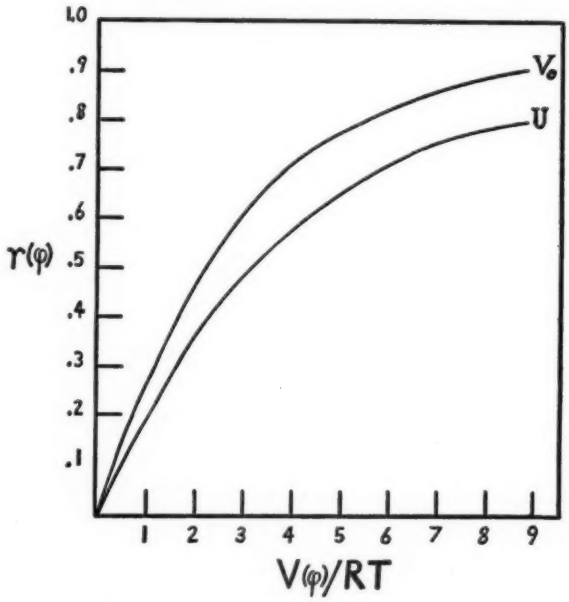

FIG. 2. Dependence of integral ratio upon potential barrier. (The identification of the abscissa should be $-r(\varphi)$.)

differing by no more than the probable error from the height of the barriers in propylene and acetone.[13] The authors do not feel the satisfaction usually exhibited over such agreement between observed and calculated values as they are cognizant of the uncertainties in the calculation of the cyanide-cyanide interaction, of the previously established incorrectness of similar calculations in the much simpler case of ethane, which points to the presence of another factor among the forces in addition to those here considered, and of the much smaller but not negligible uncertainties introduced by the solvent effect in the experimental results. It can be concluded, however, that the calculated potential barrier accounts satisfactorily for the temperature dependence of the moment of the succinonitrile molecule, while the values of this moment give an approximate value of the potential barrier.

TABLE VI. *Values (kcal.) of the potential barrier obtained from the moment values.*

	$(V(\varphi)=U)$		$(V(\varphi)=V_0(\cos\varphi+1)/2)$	
t, °C	(*a*)	(*b*)	(*a*)	(*b*)
−90	1.15	1.97	0.78	1.34
−60	1.20	1.96	.78	1.36
−30	1.09	1.99	.81	1.36
0	1.13	2.00	.82	1.30
30	1.16	1.94	.83	1.35
60	1.16	1.97	.85	1.33
90	1.19	1.93	.89	1.34

In conclusion it may be of interest to summarize for a number of 1,2-disubstituted ethanes the experimental values of the integral ratio of Eq. (6) which, by their difference from zero, give an approximate measure of the hindrance of internal rotation and, through the curves of Fig. 2, may be used to calculate the potential function and the energy barrier. The integral ratio is given in Table VII by the value of $(\mu^2/2m^2\sin^2\theta)-1$, to which Eq. (6) shows it to be equal.

Values of $(OH)_2=+0.038$, $(NH_2)_2=-0.309$, and $(CH_3CO)_2=-0.881$ might also be included in Table VII although effects other than those here considered may alter the character of the potential barriers in these molecules.

The authors wish to express their gratitude to Professor Henry Eyring for his advice as to the energy calculations and to Mr. Edward Sieminski for his collaboration in the design and construction of the apparatus.

TABLE VII. *Integral ratios for 1,2-disubstituted ethanes at 25°.*

SUBSTANCE	$(\mu^2/2m^2\sin^2\theta)-1$
$(CH_2CN)_2$	−0.340
$(CH_2I)_2$	− .735
$(CH_2Cl)_2$	− .764
$CH_2Cl\cdot CH_2Br$	− .783
$(CH_2Br)_2$	− .862

The Intermolecular Potential of Mercury

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The distribution function for liquid mercury from the melting point up to 250° recently published by the junior authors, has been used to calculate the intermolecular potential by aid of the equation derived by Hildebrand and Wood, $E=(2\pi N^2/v)\int \epsilon W r^2 dr$. This potential is accurately reproduced by the equation, $\epsilon=j/r^n-k/r^6$, with $j=5.49\times10^{-9}$ and $k=3.52\times10^{-10}$, for ϵ in dynes and r in angstroms. The attractive constant, k, checks exceedingly well with the value 3.35×10^{-10} calculated by the aid of the London formula for dispersion potential. Several other independent checks agree with the above potential function within the apparent limits of error of each.

SEVERAL years ago Hildebrand and Wood[1] published the following formula relating the potential energy of a liquid, E', to the intermolecular potential, ϵ, by the aid of the distribution function, W, yielded by x-ray scattering, which expresses the structure of the liquid:

$$E'=\frac{-2\pi N^2}{v}\int \epsilon W r^2 dr. \qquad (1)$$

N is the Avogadro number, r the distance between any pair of molecules and v the molal volume of the liquid. This equation seems to offer one of the best methods available for studying intermolecular potential since both the attractive and repulsive forces are large in the liquid state. This potential has heretofore been studied mainly through deviations from ideal gas behavior and most of the phenomena used are not very sensitive measures of the potential function.

We are now in a position to apply Eq. (1) by the aid of the data recently published by the two junior authors[2] on the x-ray scattering of mercury at seven temperatures ranging from −35°C to 250°C. We assume the simple type of potential function that has been found reasonably adequate by many others including, notably, Lennard-Jones and Devonshire[3]

$$\epsilon=\frac{j}{r^n}-\frac{k}{r^6}. \qquad (2)$$

The exponent 6 for the attractive term follows from the theoretical development by London.[4] Mercury is such a weak metal that we feel justified in neglecting the usual binding effect of metallic electrons. Anyone wishing to fit a more complicated equation to our data could readily do so, our purpose here being to give results which are illustrative rather than final. Introducing Eq. (2) into Eq. (1) gives the following expression:

$$E'=\frac{-2\pi N^2}{v}\left[j\int\frac{W}{r^{n-2}}dr-k\int\frac{W}{r^4}dr\right]. \qquad (3)$$

In order to evaluate the constants, j, k, n, we have at our disposal the energy of vaporization, ΔE, which we will assume to consist only of the change in potential energy calculated from the accurately known vapor pressure curve and the molal volume of mercury given by the density. We need only the values of the two integrals contained in Eq. (3). These have been obtained for the attractive term by plotting W/r^4 against r for each of the temperatures for which W was

TABLE I.

t°C	−ΔE kcal.	v cc	$\int\frac{W}{r^4}dr$ ×10³	$\int\frac{W}{r^7}dr$ ×10³	Calculated Liquid Potential, kcal. per mole: Attractive	Repulsive	Total	Calc.-obs. Diff.
−35	14.210	14.662	28.73	1.153	−38.05	23.81	−14.24	+0.03
0	14.095	14.756	28.05	1.113	−36.89	22.83	−14.06	−0.04
30	13.995	14.836	27.50	1.084	−35.97	22.12	−13.85	−0.15
75	13.850	14.957	26.62	1.021	−34.54	20.66	−13.88	+0.03
125	13.685	15.093	25.70	0.961	−33.05	19.28	−13.77	+0.09
175	13.520	15.230	24.65	0.897	−31.42	17.83	−13.59	+0.07
250	13.275	15.439	22.99	0.803	−28.90	15.74	−13.16	−0.12

[1] J. H. Hildebrand and S. E. Wood, J. Chem. Phys. **1**, 12 (1933).
[2] R. N. Boyd and H. R. R. Wakeham, J. Chem. Phys. **7**, 958 (1939).
[3] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. London **170A**, 464 (1939), and earlier papers.
[4] F. London, Trans. Faraday Soc. **33**, 8 (1937).

determined, as given in our former paper. The areas under the curves so plotted are given in the fourth column of Table I. The values of the three constants, j, k and n, were determined as follows: Eq. (3) was expressed as $Q=jJ-kK$, where J and K stand for the repulsive and attractive integrals, respectively, the former involving the unknown exponent, n. Using the data for three temperatures, we write

$$Q_1=jJ_1-kK_1,\ Q_2=jJ_2-kK_2 \text{ and } Q_3=jJ_3-kK_3.$$

Eliminating j and k gives the expression

$$(Q_1K_2-Q_2K_1)/(Q_2K_3-Q_3K_2) = (J_1K_2-J_2K_1)/(J_2K_3-J_3K_2).$$

The integrals represented by J values were determined graphically using values of 9, 10 and 12 for n. By using a number of sets of values, it was found that this equation yielded an approximate identity most consistently when $n=9$. The fifth column in Table I contains the repulsive integral corresponding to this exponent. Both integrals plot very smoothly against temperature. Using this exponent, and solving the resulting equations in pairs gave the following average values: $j=5.49\times10^{-9}$, $k=3.52\times10^{-10}$, corresponding to ϵ in ergs and r in angstroms. Substituting these values back in Eq. (3), with due regard to the relation between ergs and kcal., we obtain for the attractive and repulsive components of the total liquid potential the values given in columns 6 and 7. The differences between the calculated and observed values, in column 8, show the accuracy with which Eq. (3) serves to express the potential energy of the liquid. These three sets of values are plotted against temperature in Fig. 1. The potential between a pair of mercury atoms in terms of Eq. (2) is plotted in Fig. 2.

The following evidence is available for testing the validity of this particular potential function.

(1) The minimum potential occurs at 2.87A, which agrees closely with the lattice constant for solid mercury, 3.00A at $-46°$.[5]

(2) The minimum distance between any appreciable number of mercury atoms in the liquid is given by the x-ray scattering as approximately 2.4A. The mean kinetic energy of mercury atoms

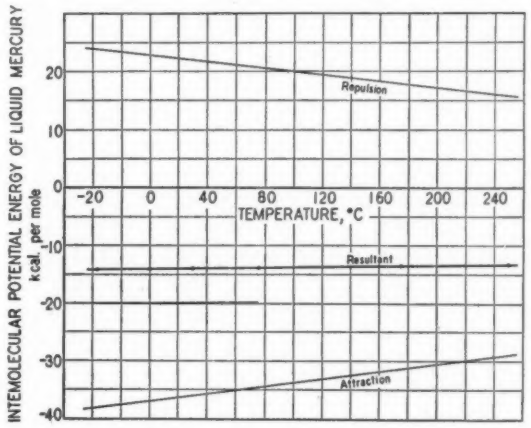

FIG. 1.

at 200°C is 9.7×10^{-14} erg which, according to the potential curve, would permit an approach to within 2.6A and an appreciable proportion of the atoms at this temperature would have energy enough to reduce the distance to about 2.5A, which is as close an agreement with the initial portion of the probability curve as we have any right to expect.

(3) The dispersion theory of London gives the following approximate expression for the attractive energy between nonpolar molecules,

$$\epsilon=\frac{3\alpha^2V}{4\pi r^6}, \tag{4}$$

where α is the polarizability and V is a potential somewhere between the limits of excitation and ionization. The latter is 10.38 volt-electrons. We have calculated α from the measurements of the refractive index of mercury vapor made by G. Wolfsohn.[6] These measurements extend over a sufficient range of wave-length so that we can extrapolate to infinite wave-length to get 1.00088, which gives a polarizability of 5.2×10^{-24}. Substituting in Eq. (4) gives for the coefficient of $1/r^6$ the value 3.35×10^{-10}, which agrees with the previously found value of k, 3.52×10^{-10}, far more closely than either method would give us any right to expect.

(4) A study of the spectra of mercury has revealed the existence of double molecules of mercury. These molecules are attributed solely

[5] M. C. Neuberger, Zeits. f. anorg. allgem. Chemie **212**, 40 (1933).

[6] G. Wolfsohn, Zeits. f. Physik **63**, 634 (1930); **83**, 234 (1933).

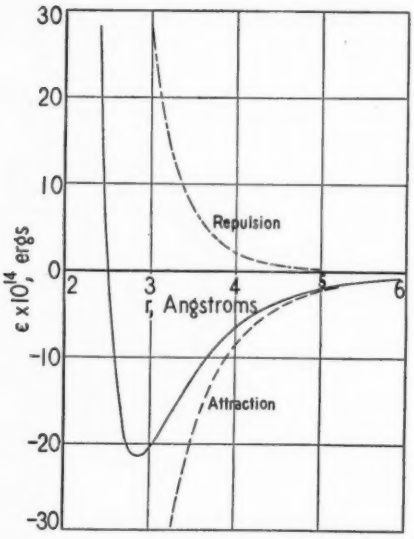

FIG. 2.

to dispersion forces and are therefore not to be expected to persist as such in larger aggregates in the liquid state. Several observers[7] have calculated the energy of dissociation of Hg_2 molecules. Their values are from 1.4 to 1.6 kcal. per mole but are subject to considerable uncertainty, given by one observer as 0.3 and another as 0.7 kcal. per mole. The value 1.6 corresponds to 11×10^{-14} erg per molecule pair which, in view of its uncertainty, may be regarded as sufficiently close to our minimum potential of 21×10^{-14} erg.

(5) A theory of specific heat published by Meshcherskii[8] is expressed in an equation containing a term corresponding to the minimum potential of a pair of mercury atoms of 28×10^{-14} erg, which is probably as close as can be expected to our 21×10^{-14} erg.

(6) The Joule-Thompson effect and the second virial coefficient of gases have frequently been used to derive intermolecular potential functions but such data are not available in the case of mercury vapor. The viscosity of the vapor, however, has been applied to this end by H. R. Masse and W. R. Cook.[9] The solution of the theoretical equation derived by these authors was simplified by the selection, rather arbitrarily, of exponents 4 and 8, respectively, for the attractive and repulsive potential terms. The coefficients derived for their equation yield a minimum in energy at 2.05A, a value entirely too small in view of the interatomic distance in both liquid and solid mercury. Their expression also gives a value for the potential at 3A of 13×10^{-14} erg, considerably less than our 21×10^{-14} erg. It would be interesting to see how well our own potential function substituted back in the viscosity equation would reproduce the experimental viscosities.

We shall call attention at this time to only a few of the numerous deductions possible from such a potential function.

The repulsive potential for mercury is less steep than it is for certain harder molecules such as He, Ne, A, with their more tightly bound electrons, and the error that would be made by the simplifying assumption of hard spheres would be considerable.

The lively interest now being shown in the nature of the melting process, has directed attention to the problem of a statistical formulation of the attendant increase in entropy. This has usually been attempted by treating the liquid as a quasi-solid, consisting of a lattice of mean positions as in a solid, and differing only in being more mussed up and by having certain lattice points unfilled or in approaching a lattice of lower coordination number. Our formulation of the energy suggests, we believe, a less artificial approach. The change from solid to liquid is described in a concrete, physical sense by the change from a discontinuous to a continuous distribution function.[10] The latter describes what is essential to a liquid, much as a wave function describes all that is essential to the behavior of an electron. We have learned that is both futile and unnecessary to try to assign instantaneous locations to electrons and we contend that the same is true of the molecules of a liquid. The entropy of a dilute gas is $R \ln V+\text{const.}$, a continuous function, and the entropy of a liquid must be expressed in some analogous way rather than in terms of a probability expressed in terms of a finite number of configurations.

[7] Finkelnberg, Physik. Zeits. **34**, 551 (1933); Koernicke, Zeits. f. Physik **33**, 219 (1925); Kuhn and Freudenberg, Zeits. f. Physik **76**, 38 (1932); Mrozowski, Zeits. f. Physik **104**, 230 (1936). Cf. Acta Physica Polonica **3**, 215 (1934); Zeits. f. Physik **106**, 458 (1937).

[8] B. A. Meshcherskii, J. Russ. Phys. Chem. Soc., Phys. Pt. **61**, 179 (1929). Cf. C. A. **24**, 4984 (1930).

[9] H. R. Masse and W. R. Cook, Proc. Roy. Soc. London **125A**, 196 (1929).

[10] Cf. reference 1, Fig. 1B.

Inversion of the Partition Function to Determine the Density of Energy States*

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The density of energy states for a complex system may be deduced from thermodynamic functions when their dependence on temperature is specified. The method is general and depends for its accuracy on the closeness of approximation of the experimentally determined partition function by an appropriate equation. Accurate specific heat data are therefore essential. The degeneracy function is obtained by inverting the Laplace integral defining the sum-over-states; as illustrations, the energy states for an Einstein crystal, and for a modified Debye crystal without and with a transition are discussed. The author was not successful in finding a mathematical expression which fitted the last case sufficiently well to differentiate between transitions of first and higher order.

OF importance to any theory of molecular structure is a general procedure for locating the position and estimating the degeneracy of the characteristic energy states, applicable equally well to simple and complex molecules, crystals and liquids. As examples of recent interest, for which at the outset of any discussion, some form of the degeneracy function must be assumed, one may list the following two types. (a) Order-disorder transitions, often accompanied by λ phenomena; (b) transitions to the superconducting state, and the analogous phase change from liquid helium I to II. Since many investigators are concerned with these problems, it appeared worth while to study the possibilities of a very general method suggested previously by the author.[1] It is based on the use of thermodynamic functions, and is essentially the inverse of the current procedure of computing thermodynamic properties from spectral data.

The sum-over-states may be readily obtained as a function of the temperature from the experimentally determined entropy,

$$\frac{1}{N}\log Z(T)=\frac{1}{RT}\int_0^T S(T)dT + \frac{1}{N}\log G_0 e^{-E_0/kT} - \frac{9}{8}\frac{h\nu_m}{kT}.$$

The last two terms of the right member must be added to allow for the zero-point energy ($-9h\nu_m/8kT$, for a Debye crystal) and for the degeneracy of the basic state which is used as the reference level from which the energy spectrum is to be measured. On the other hand, a fundamental definition of quantum statistical mechanics relates the sum-over-states to the degeneracy function of the energy levels of the system as a whole,

$$Z(T)=\sum_m G(E_m)e^{-E_m/kT}. \quad (1)$$

The problem is then reduced to an inversion of (1) so that the density $G(E_m)$ could be found once a $Z(T)$ is given. If one does not restrict $G(E)$ to the class of continuous functions, it is permissible to replace the summation by an integration even when discrete states are indicated. This will be illustrated by a discussion of the Einstein model for a crystal. The degeneracy function may then be obtained by inverting the Laplace integral equation, for a continuum of energy levels,

$$Y(x)\equiv Z(h\nu_m/kx)=h\nu_m\int_0^\infty G(E)e^{-xE}dE; \quad (2a)$$

or the Stieltjes integral equation, for a set of discrete states,

$$Y(x)=h\nu_m\int_0^\infty e^{-xE}dH(E);$$

deduced from (1) through the change of variable $T=h\nu_m/kx$, so that both E and x are dimensionless. Clearly, a rigorous solution is not feasible

* This discussion was presented, in part, at the Baltimore meeting of the American Chemical Society.

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[1] S. H. Bauer, J. Chem. Phys. **6**, 403 (1938).

since the partition function cannot be evaluated from experimental data for values of x approaching zero. The closeness of approximation will depend on how well the mathematical expression used for $Y(x)$ represents the actual sum-over-states; here is the one limiting feature of the method. It is not only necessary to have a good fit over the known range but it is essential to use a function which approaches infinity at $x=0$ and vanishes for $x\to\infty$ in the correct manner. The uniqueness of the solution will depend on whether the representation is unique; in general that is not the case.

The restrictions which are imposed on the function $G(E)$ to permit the Laplace inversion have been extensively discussed. They are sufficiently broad to include all cases which have physical reality insofar as partition functions are concerned. Thus, if (a) the real function $g(E)$ and its first derivative are piecewise continuous; (b) at a point of discontinuity $g(E)=\frac{1}{2}\times[g(E+0)+g(E-0)]$; and (c)

$$\int_0^\infty |g(E)|\,e^{-cE}dE$$

exists for c a real constant greater than zero, then $g(E)$ may be represented by the complex integral

$$g(E)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{f(x)}{x}e^{xE}dx, \tag{3}$$

where

$$f(x)=x\int_0^\infty g(E)e^{-xE}dE, \tag{4}$$

and defines an analytic function in the half-plane.[2] We have then a solution for (4) in terms of the contour integral (3). Another form in terms of the derivatives of $f(x)$ for large real positive values of x has been developed by Widder.[3] We shall use the results derived by either method as convenience dictates.

[2] For a discussion of the general case see H. Hamburger: Math. Zeits. **6**, 6 (1920).

[3] Restricting conditions and an inversion formula are given: D. V. Widder: Trans. Am. Math. Soc. **36**, 107 (1934). For the more general Laplace-Stieltjes integral, $f(x)$ need not be analytic; it is necessary and sufficient that $f(x)$ have derivatives of all orders and that integrals of the type $\int_x^\infty \frac{u^k}{k!}|f^{(k+1)}(u)|\,du$ are bounded. See p. 151.

Details of the Inversion

To facilitate the discussion of the solutions for (2a, b) let us consider several specific forms for $Y(x)$. Experience has shown that partition functions generally may be expressed as sums of terms involving e^{-ax} and $e^{-ax}f(x)$ [where $f(x)$ is restricted to forms of the types quoted below]. Hence the solutions $G(E)$, $H(E)$ may be compounded of solutions of (5) and (6), weighted by the corresponding coefficients of the expansion.

$$e^{-ax}f(x)=\int_0^\infty G(E)e^{-xE}dE; \tag{5}$$

$$e^{-ax}=\int_0^\infty dH(E)e^{-xE}. \tag{6}$$

The solution of the first of these is given by a general theorem of the Heaviside operational calculus,[4] *viz., If two functions, $f(x)$ and $g(E)$, are so related* [indicated by the symbol $f(x)\doteqdot g(E)$] *that they satisfy the equation*

$$f(x)=x\int_0^\infty g(E)e^{-xE}dE,$$

then

$$e^{-ax}f(x)\doteqdot\begin{cases}0 & \text{for } E<a\\ g(E-a), & \text{for } E>a\end{cases}\quad\text{with } a>0. \tag{7}$$

We now quote several transforms which will be useful for the applications suggested in this paper.

$$1\doteqdot h(E)\quad\text{where } h(E)=\begin{cases}1 & \text{for } E>0,\\ 0 & \text{for } E<0,\end{cases} \tag{8a}$$

$$x^{-n}\doteqdot E^n/\Gamma(n+1)\quad\text{for all } n \text{ except negative integers,} \tag{8b}$$

$$1/(x+\alpha)\doteqdot(1-e^{-\alpha E})/\alpha, \tag{8c}$$

$$x/(x+\alpha)^n\doteqdot e^{-\alpha E}E^{(n-1)}/(n-1)!,^5 \tag{8d}$$

$$x/(x+\alpha)(x+\beta)\doteqdot(e^{-\beta E}-e^{-\alpha E})/(\alpha-\beta). \tag{8e}$$

[4] The Heaviside operational calculus is almost exclusively based on the Laplace transform by means of the contour integral. A concise review by Louis A. Pipes appeared in the J. App. Phys. **10**, 172, 258, and 301 (1939). A long list of transforms is given from which the ones quoted in the text have been taken.

[5] Contrast (8d) with

$$\frac{wx}{w^2+(x+\alpha)^2}\doteqdot e^{-\alpha E}\sin wE\quad\text{for}\quad\begin{cases}n=2\\ w^2\ll 1.\end{cases}$$

The difference between the left members would hardly be noticeable experimentally, yet the forms of the two solutions are radically different. This demonstrates the lack of uniqueness mentioned above. For the applications suggested, the sinusoidal solution is not admissible.

Integrations by parts and successive differentiation of the Laplace integral equations corresponding to (8a–e) lead to more general transforms;[6] solutions for functions which are combinations of the left members also may be obtained. Thus,

$$\textit{If } f_1(x) \doteqdot g_1(E) \textit{ and } f_2(x) \doteqdot g_2(E), \textit{ then}$$

$$f_1 f_2 \doteqdot \frac{d}{dE}\int_0^E g_1(E-u)g_2(u)du; \qquad (9)$$

so that

$$[f_1(x)]^2 \doteqdot \frac{d}{dE}\int_0^E g_1(E-u)g_1(u)du.$$

Generalization of these relations for the Nth power of $f_1(x)$ is obvious.

The contribution due to the discrete energy states is deduced in a straightforward manner from the more general Laplace-Stieltjes Eq. (6). The solution as given by Widder[3] expresses the function $H(E)$ as the limit of

$$H(E)=\lim_{k\to\infty} e^{-ak/E}\sum_{p=0}^{k}\frac{1}{(k-p)!}(ak/E)^{k-E}$$

$$=\begin{cases}0 & \text{for } 0<E<a\\ \frac{1}{2} & E=a\\ 1 & a<E<\infty\end{cases}; \text{ Fig. 1.} \qquad (10)$$

To clarify the meaning of the Stieltjes integral and to demonstrate that the suggested procedure leads to the correct result, let us consider an Einstein crystal, for which

$$[Y(x)]^{1/N}=\frac{e^{-3x/2}}{(1-e^{-x})^3}=\sum_{n=0}^{\infty}\binom{n+2}{n}e^{-(\frac{3}{2}+n)x}$$

$$=h\nu_0\int_0^{\infty}e^{-x\epsilon}d\left[\sum_n\binom{n+2}{2}H_n(\epsilon)\right];$$

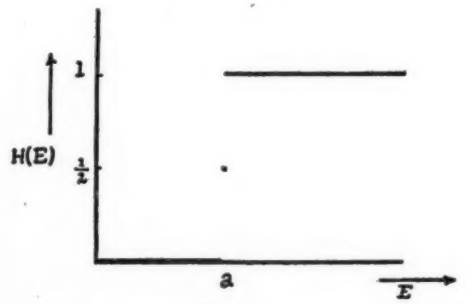

FIG. 1.

[6] Six theorems are discussed by Pipes. His exposition proved very helpful to the author, and sincere acknowledgment is here made.

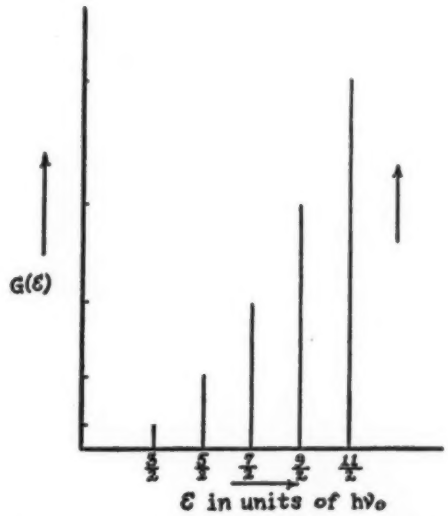

FIG. 2. The density of energy states for an Einstein crystal.

where $x=h\nu_0/kT$, ν_0 denotes the characteristic frequency, and ϵ_n the energy levels of a single oscillator. It is permissible to write the sum-over-states in terms of ϵ_n rather than E_m (energy levels of the system as a whole) whenever the system is composed of N similar, weakly interacting elements which are permanently distinguishable; such is the case here. As is explicitly indicated, for each value of n there is a solution $H_n(\epsilon)$ weighted by the corresponding binomial coefficient, and the degeneracy function is the sum of these. From (10),

$$H_n(\epsilon)=\begin{cases}0 & 0<\epsilon<(\frac{3}{2}+n)\\ \frac{1}{2} & \epsilon=(\frac{3}{2}+n)\\ 1 & (\frac{3}{2}+n)<\epsilon<\infty.\end{cases}$$

In contrast to Eq. (5), in which values of a function of E at particular values of the argument, are multiplied by increments of the argument and then summed as these increments are made to approach zero, the Stieltjes integral equation (6) requires that one multiply values of the function of ϵ by increments in another function $H(\epsilon)$ computed at the chosen points, and sum as $\Delta H(\epsilon)\to 0$. Hence, corresponding to the degeneracy function $G(E)$, is the limit

$$\lim_{\sigma\to 0}[H_n(\epsilon+\sigma)-H_n(\epsilon-\sigma)]=\begin{cases}0 & \epsilon<(\frac{3}{2}+n),\\ 1 & \epsilon=(\frac{3}{2}+n),\\ 0 & \epsilon>(\frac{3}{2}+n).\end{cases}$$

This is clear from Fig. 1. The position of the energy levels is then given by $\epsilon=(\frac{3}{2}+n)$, and

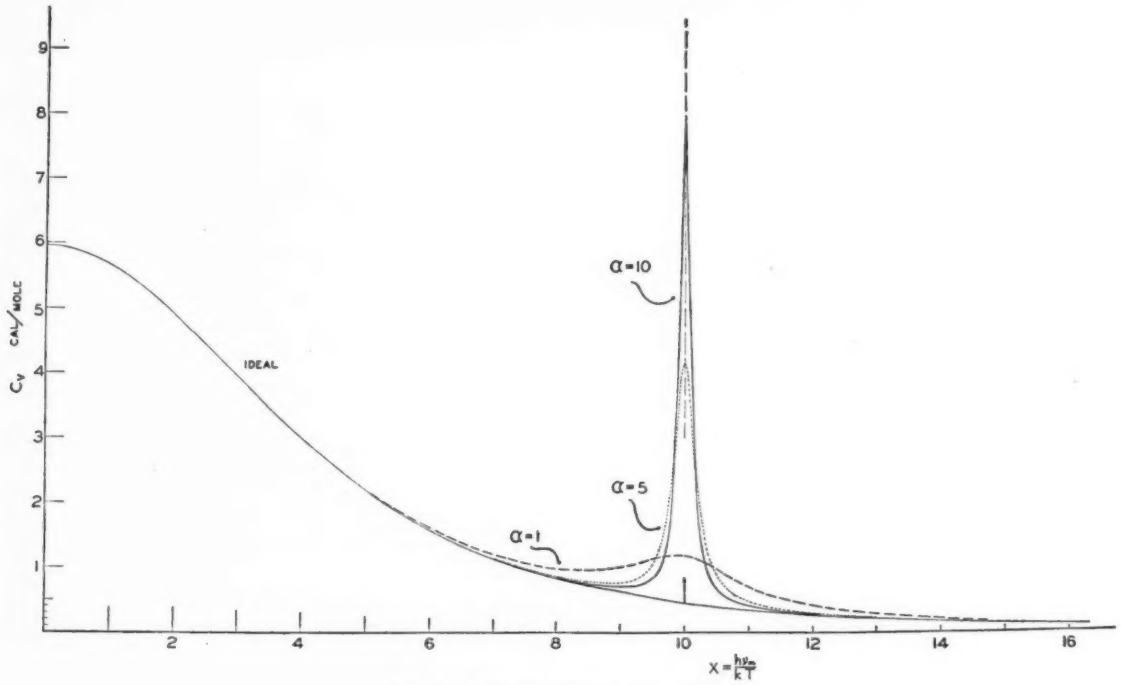

FIG. 3. Modified specific heat curves.

their degeneracy by $\binom{n+2}{n}$, which is the expected result;[7] Fig. 2.

That the representation of the experimentally determined partition function is not unique, even though the limiting conditions are satisfied has been indicated above. One must therefore rely on physical intuition as a guide to the acceptable forms.[8] For most systems, the sum-over-states may be represented to within the experimental error by sums of functions for which the transforms can be deduced through the application of the theorems given by Pipes[4] to (8a–e) and like terms.

SENSITIVITY OF THE METHOD

To gauge the sensitivity of the method, we studied the following model. To the specific heat of a Debye crystal,

$$C_v(x)=\frac{36R}{x^3}\int_0^x \frac{z^3dz}{e^{-z}-1}-\frac{9Rx}{e^x-1},$$

we added

$$C_t(x)=A/(1+\alpha^2(x-x_0)^2); \qquad (11)$$

a hump at x_0, rounded and of finite width, to *simulate* the type of maximum observed during a phase change of second order. The curves shown in Fig. 3 are of the modified specific heats as

TABLE I. *Let* $W(x)=y(x)e^{-9x/8}$.

x	$W(x)$ IDEAL*	$W(x)_r$ EQ. (13)	$W(x)_t$ IDEAL +TRANS. $\alpha=1$	$\alpha=10$	$\alpha=\infty$	$W(x)_{t,r}$ EQ. (14) $\alpha=\infty$
0.2	423.67	423.14	477.66	475.32	475.30	475.29
.4	65.824	66.431	73.818	73.699	73.624	74.335
.6	24.070	24.354	26.883	26.869	26.869	27.240
.8	12.453	12.557	13.859	13.874	13.874	14.073
1.0	7.7974	7.8133	8.6477	8.6616	8.6624	8.7500
1.5	3.6877	3.6911	4.0588	4.0718	4.0730	4.1035
2	2.4042	2.4085	2.6274	2.6388	2.6398	2.6396
5	1.1480	1.1458	1.2082	1.2162	1.2170	1.2168
6	1.0909	1.0873	1.1337	1.1400	1.1408	1.1412
9	1.0283	1.0266	1.0406	1.0403	1.0404	1.0458
10	1.0196	1.0194	1.0255	1.0210	1.0196	1.0334
11	1.0146	1.0146	1.0177	1.0150	1.0146	1.0248
15	1.0059	1.0058	1.0066	1.0060	1.0059	1.0088

* These values were taken from the tables of F. H. MacDougall, *Thermodynamics and Chemistry* (Wiley and Sons, New York, 1926). The parameters of the Eqs. (13), and (14) were obtained by a method of successive approximations. Better fitting than the above is possible, but laborious.

[7] The weight of the excited states of an Einstein crystal is given by the number of ways of placing n quanta into three groups; that is, the excitation of a three-dimensional harmonic oscillator: $\frac{(3+n-1)!}{n!(3-1)!}$.

[8] The types of equations suggested by G. M. Murphy (J. Chem. Phys. **5**, 637 (1937)) and by J. W. Linnett and W. H. Avery (J. Chem. Phys. **6**, 686 (1938)) cannot be used for the present purposes since they do not satisfy the necessary limiting conditions.

functions of x, for $x_0=10$ and $\alpha=1, 5, 10$ and ∞, the latter representing a phase change of the usual type. For purposes of computation we have taken the area under C_t approximately equal to that under the Debye curve from infinity to x_0; that is,

$$\frac{A\pi}{\alpha}=\frac{12\pi^4R}{5}\int_{x_0}^{\infty}\frac{dx}{x^3}=1.2\pi^4\frac{R}{x_0^2}. \qquad (12)$$

Further, we imposed the condition that as α is made to approach infinity, the area is to remain constant. Thus the limiting case of the specific heat curves typifying a transformation similar to that of second order is one with a sharp transition involving the same total heat effect. From these we deduced the entropy and the sum-over-states, and hoped to fit the $Y(x)$ sufficiently well to distinguish these functions for various values of α. It would thus be possible to determine the manner in which the density of energy states changes as α approaches infinity.

It was only after investigating numerous func-

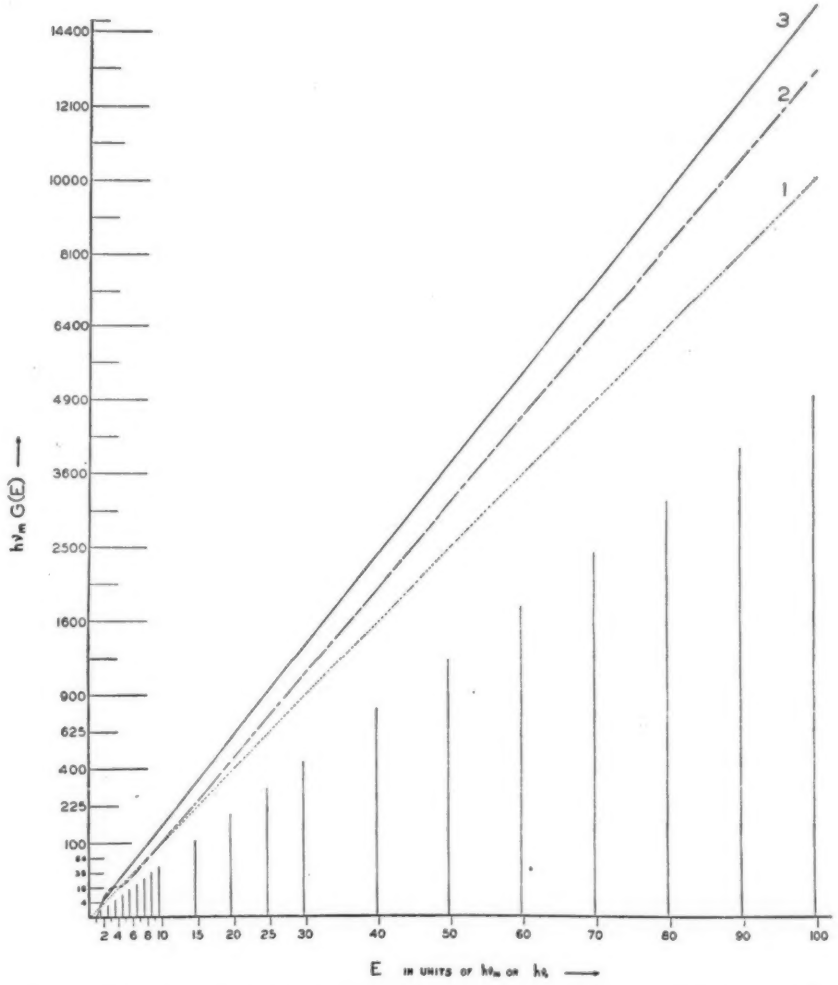

FIG. 4. The energy is plotted along the abscissa in units of $h\nu_m$ for curves (2) and (3), or units of $h\nu_0$ for the vertical lines. Note that the ordinate is a squared scale and gives, respectively, $h\nu_m G(E)$ or $h\nu_0 G(\epsilon)$. For comparison, the dotted line (1) relates

$$\text{ordinate}=[\text{abscissa}]^2.$$

Curve (2) is the solution of the integral equation corresponding to (13) and specifies the density of energy states for the pseudo Debye crystal; Curve (3) corresponds to (14)— for the pseudo Debye crystal with a sharp transition at $x=10$. The vertical lines, most of which have been omitted, are the energy density spectrum for an Einstein crystal.

tions that a representation was found which had the proper limiting conditions and agreed with the known $[Y(x)]^{1/N}$ values for the ideal crystal and for the superposed transition to within several tenths of a percent. The computations are relatively simple when the Nth root of the partition function is dealt with, but become very cumbersome when the sum-over-states for the system as a whole has to be manipulated. To facilitate the computations for this test case, we arbitrarily replaced the Debye crystal by N similar but weakly interacting subsystems, and the degeneracy function was evaluated for the energy levels of the smaller units. Thus we have replaced $[Y(x)]^{1/N}$ by $y(x)$, and considered the latter as the sum-over-states. Reference to Table I shows that the errors introduced using the equations given below are larger than the differences between the $y(x)e^{9x/8}$ values for the various α's, although in absolute magnitude they are of the same order as those introduced by the specific heat measurements; values for a crystal without and with a transition are clearly distinguished. For the pseudo Debye crystal we assumed

$$y(x)_r = e^{-9x/8}\left(1+\frac{a(x)}{x^3}-b(x)\right),$$

where

$$a(x) = 19.4818 - 16.7635(e^{-0.66x} + e^{-0.73x} - e^{-1.237x}),$$
$$b(x) = \frac{17.5x+1}{(x+1)^3}e^{-1.07x}. \tag{13}$$

For this pseudo Debye crystal with a sharp transition at $x=x_0$ ($\alpha=\infty$), the same form for $y(x)_r$ was assumed but

$$a(x) = 19.4818 - 16.4264(e^{-0.66x} + e^{-0.73x} - e^{-1.204x}),$$
$$b(x) = \frac{7.2x+1}{(x+1)^3}e^{-0.25x} - \frac{26x}{(x+2.4)^3}e^{-0.2x}. \tag{14}$$

To take the restrictions at $x=0$ into consideration, for α finite, the form of $a(x)$ in (14) was modified;

$$a(x) = 19.4818 - (1.1241x^{-\epsilon} - 17.5505) \times (e^{-\rho x} + e^{-\sigma x} - e^{-\lambda x}),$$

where

$$\epsilon = \frac{1.2\pi^3}{x_0^2}\frac{\alpha}{1+\alpha^2 x_0^2}.$$

Solutions for the integral equations corresponding to the above forms of $y(x)_r$ follow from the application of (7) to (8b, c, d); the consequent degeneracy functions for this pseudo Debye crystal without and with a sharp transition are plotted in Fig. 4, in units of $h\nu_m$.

Acknowledgments

I wish to express my sincere appreciation to Dr. J. L. Justice who performed a large part of the computations involved in the curve fitting, and to Professor I. M. Sheffer for several helpful discussions regarding some of the mathematical aspects of this paper.

Kinetics of Phase Change. I*

General Theory

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The theory of the kinetics of phase change is developed with the experimentally supported assumptions that the new phase is nucleated by *germ nuclei* which already exist in the old phase, and whose number can be altered by previous treatment. The density of germ nuclei diminishes through activation of some of them to become *growth nuclei* for grains of the new phase, and ingestion of others by these growing grains. The quantitative relations between the density of germ nuclei, growth nuclei, and transformed volume are derived and expressed in terms of a *characteristic time scale* for any given substance and process. The geometry and kinetics of a crystal aggregate are studied from this point of view, and it is shown that there is strong evidence of the existence, for any given substance, of an *isokinetic* range of temperatures and concentrations in which the characteristic kinetics of phase change remains the same. The determination of phase reaction kinetics is shown to depend upon the solution of a functional equation of a certain type. Some of the general properties of temperature-time and transformation-time curves, respectively, are described and explained.

A. INTRODUCTION

IN the appearance of a new phase from a previous one upon change of temperature, concentration, or other controlling factors, there is almost always the possibility of a lag or "metastable" condition beyond the equilibrium point. If, for the sake of specificity, we suppose temperature to be the controlling factor, and maintain other external conditions constant, we may describe the general phenomena as follows. Upon lowering the temperature slightly below the equilibrium point, and maintaining it there, the new phase sets in at a rate first slow, then faster, and finally toward the end of the transformation, slow again. The general S-shape of the transformation-time curve is characteristic of such changes at lower "supercooling" temperatures also, and any adequate theory must account for it quantitatively. As the temperature at which the transformation-time curve is determined is progressively taken lower, the time required for any given amount of transformation is found to be shorter until a minimum is reached. This temperature of very rapid rate, in the case of crystallization from solutions and melts, probably corresponds with the temperature of "supersolubility" and "superfusion" considered by Ostwald[1] and Miers.[2] Whether, upon further lowering of the supercooling temperature, the time for the transformation is increased again depends upon other factors, primarily, as we shall see below, upon the "rigidity" of the phases involved with respect to the movements of the constituent particles. As an instance, with industrial importance, of the temperature-time curves of this sort, we may take the upper part of the hardenability governing "*S* curve" (not to be confused with the S-shape of the general transformation-time curves) of a simple carbon steel given in Fig. 1.[3] The lower part of this curve depends upon other complex factors which will be considered in detail elsewhere.

Two other groups of experimental data bearing on phase transformation are sometimes available. First, the number of growth nuclei of the new phase formed as a function of time may be observed. For transparent media this may often be done by direct count; for opaque media, by "freezing" the situation at a given stage of the transformation, cutting through the material, and, with the aid of polishing or etching techniques (as in metallography), determining the nuclear count in the exposed surface. Second, in similar ways, the frequency of grains of a given size at any stage of the transformation may be determined. In all the experiments in which the data are taken by inspecting the surface of a cut through the material, it must

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] W. Ostwald, *Lehrbuch der Allgemeinen Chemie*, Vol. II, Part 2, p. 780.

[2] H. A. Miers, J. Chem. Soc. **89**, 413 (1906); Proc. Roy. Soc. **A79**, 322 (1907).

[3] E. S. Davenport and E. C. Bain, Trans. American Institute of Mining and Metallurgical Engineers, Iron and Steel Division **90**, 117 (1930). E. C. Bain, **100**, 13 (1932).

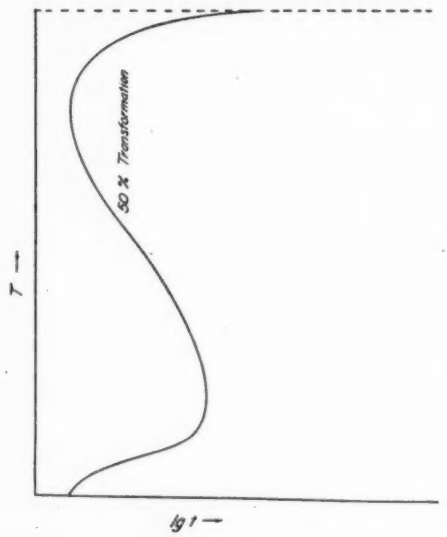

FIG. 1.

be remembered that the surface is a random one, and the actual space frequency-size distribution must be deduced by statistical methods from the observed one. Methods for doing this have been given by Huber[4] and Scheil.[5]

Numerous investigations, both theoretical and experimental, have been made of the mechanism of phase change. There is an overwhelming amount of evidence pointing to the conclusion that the new phase is nucleated by tiny "germ nuclei," or "ultra-nuclei," which already exist in the old phase, and whose effective number can be altered by temperature and duration of superheating. These may consist of heterogeneities of any type, e.g., foreign particles with an adsorbed layer of the new phase, or tiny "blocks" or "crystal molecules" of the new phase (if solid) of the sort contemplated in one form or another by Zwicky, Smekal, Goetz, and many others.* In accord with the Gibbs-Thomson relation between vapor pressure and particle size, such germ nuclei will have a lower transition temperature than grains of larger size. Nevertheless, the kinetic reasoning of Bloch, Brings, and Kuhn[7] (in the case of crystals) indicates that, for given supercooling or superheating, they grow or diminish considerably more slowly than grains of visible size. It would be highly desirable to have this theory placed on a more fundamental basis.

Whatever the hypothesis as to their nature, the existence of these nuclei is so well established that to ignore it in a theory of the kinetics of phase transformation is to open the way to gross discrepancy with the experimental data. The two attempts to deal with the kinetics of isothermal crystallization and solid-solid phase change by Göler-Sachs†[8] and Mehl-Johnson[9] are open to this objection. They effectively assume, following Tammann,[10] a constant rate of spontaneous nucleation of the new phase either throughout (and proportional to) the volume, or upon the grain surfaces, of the old phase. This spontaneous rate of nucleation is a function of temperature and can be determined following Volmer and others,[11] from thermodynamic considerations. We shall discuss this matter more fully elsewhere. In the meantime we may note that the assumption of constant rate of nucleation (proportional to the transforming volume or surface) is in very many cases definitely contradictory to the experimental facts. The work of deCoppet,[12] Hammer,[13] Scheil-Lange-Weise[14] and

[4] A. Huber, Zeits. f. Physik **93**, 227 (1935).

[5] E. Scheil, Zeits. f. Anorg. allgem. Chemie **201**, 259 (1931); W. Bading, E. Scheil and E. H. Schulz, Arch. Eisenhüttenwes. **6**, 69 (1932/33); E. Scheil and H. Wurst, Zeits. f. Metallkunde **28**, 340 (1936).

* A review of the experimental work bearing upon the nature of such block structures of crystals can be found in a book by Desch (reference 6) and in the report on the Solid State at the International Conference on Physics (1934). *Note added in proof.*—An interesting possibility is that some of these germ nuclei are "heterophase fluctuations," present from above the equilibrium temperature, of the type recently considered by Frenkel (J. Chem. Phys. **7**, 538 (1939)). This possibility, examined quantitatively, leads to the result that the apparent probability of nucleation n of such germ nuclei increases with time up to a maximum after which it becomes constant. This may account for the fact that sometimes the rate of appearance of growth nuclei seems first to increase to a maximum before dropping off in accord with the simple theory where n is supposed constant.

[6] C. H. Desch, *The Chemistry of Solids* (Cornell University Press, 1934).

[7] R. Bloch, T. Brings, and W. Kuhn, Zeits. f. physik. Chemie **12B** 415 (1931).

† See also Huber (reference 4).

[8] F. v. Göler and G. Sachs, Zeits. f. Physik **77**, 281 (1932).

[9] R. F. Mehl, "The Physics of Hardenability," Symposium on Hardenability, American Society of Metals, Detroit, October, 1938.

[10] G. Tammann, *Kristallisieren und Schmelzen* (Leipzig, 1903).

[11] M. Volmer and A. Weber, Zeits. f. physik. Chemie **119**, 277 (1926); M. Volmer and M. Marder, Zeits. f. physik. Chemie **A154**, 97 (1931).

[12] L. C. de Coppet, Ann. Chem. et phys. **8: 10**, 457 (1907).

[13] C. Hammer, Ann. d. Physik **33**, 445 (1938).

[14] E. Scheil and H. Lange-Weise, Archiv Eisenhüttenwesen **11**, 93 (1937/38).

others, indicates that, as transformation proceeds, the rate of observed nucleation decreases much faster than in proportion to the untransformed region, so that the total number of growth nuclei approaches a definite saturation value characteristic of the degree of undercooling. It is as though only a certain number of germ nuclei which, becoming activated, can serve as nuclei for growth to grains of observable size, are originally present, and as transformation proceeds these become used up. Why the total number of growth nuclei which appear depends upon the temperature of supercooling, we shall see later.

The second assumption, which Göler-Sachs and Mehl-Johnson make in their analyses, deriving also from Tammann, i.e., that of the constant rate (at a given temperature) G of linear increase of a crystal from a growth nucleus, is well verified by experiment for macroscopic crystals. It is evidently equivalent to the assumption that the rate of volume growth of the crystal is proportional to its surface area (for constant shape). For extremely small crystals this relation must probably be modified as suggested before.

Putting the two assumptions discussed above together, one can derive an expression for the rate of transformation of the matter from the old phase to the new. Göler-Sachs, working with the case of volume nucleation, derive an approximate expression assuming the growing grains to be spheres and neglecting the slowing down effect due to the impingement of grains upon each other and the cessation of growth in the overlapping regions. Mehl-Johnson claim to follow a similar method, though modified to the case of surface nucleation (for the austenite-pearlite transition in silicon killed steels) and corrected for the overlapping of the growing spheroids. They indicate only the results, the derivation to be published later. In both cases, however, as is to be expected from the incorrectness of one of the fundamental assumptions, the results do not fit experiment. Thus, for instance, one conclusion which should follow from the assumption of constant rates of nucleation and growth is that the distribution curve for frequency with grain size when the transformation is complete, should practically be a horizontal straight line. Instead, as the data of Tammann-Crone[15] on cadmium and aluminum, and of Scheil-Lange-Weise on the austenite-pearlite transition show, the frequency-size curve is concave to the abscissa, rising from zero for the largest size to a maximum and dropping to zero again. Thus there are actually far fewer small crystals than is to be anticipated on the basis of the constant nucleation hypothesis. This fact is of course consistent with the idea that the germ nuclei which serve as the basis of the growth nuclei get used up as the reaction proceeds. The apparent abnormal smallness in the number of very large grains is probably due to the above-mentioned difference between the frequency-size distribution on a random surface and the actual space frequency-size distribution. We shall allow for this later.

The above and related considerations lead us to adopt the following simple picture, which, we shall show in the sequel, accounts quantitatively for many of the phenomena of phase change. We shall also see that it leads, in one extreme case, to the assumptions which underlie the Göler-Sachs analysis. It thus includes the latter as a special case.

B. Relation Between Germ Nuclei, Growth Nuclei and Transformed Volume

Let us suppose that there were $\bar{N}$ germ nuclei distributed in any manner whatsoever per unit volume and present from above the equilibrium temperature. These consist either of small blocks of the subcritical phase or tough films of the latter surrounding foreign inclusions. At any rate, $\bar{N}$ is a function of the time and temperature of superheating, generally decreasing with increase of either.

During transformation the germ nuclei get used up and their number per unit volume $N \equiv N(t)$ decreases from $\bar{N}$ in two ways. First, some of them become active growth nuclei (whose number we represent by $N' \equiv N'(t)$) in consequence of free energy fluctuations (which may come from size, concentration, or order fluctuations in the various possible cases) which enable them to jump over the boundary of the metastable region. The probability of this happening is given by nN where $n \equiv n(T)$, the

[15] G. Tammann and W. Crone, Zeits. f. anorg. Chemie **187**, 289 (1930).

probability of formation of growth nuclei per germ nucleus per unit time, may be calculated as a function of temperature by methods similar to those of Volmer, Stranski-Kaischew,[16] Borelius,[17] and Becker.[18] It will have the general form*

$$n(T)=Ke^{-Q+A(T)/RT},$$

where Q, a constant, is an energy of activation (per gram molecule), R is the gas constant, and $A(T)$ is the work per gram molecule required for forming a growth nucleus at temperature T. Volmer and Weber[11] have demonstrated that a growth nucleus forming at an interface requires less work than one forming within a phase. Thus A is smaller and n larger at such an interface. It is to this fact that we may ascribe the formation of growth nuclei about germ nuclei long before spontaneous nucleation within the phase is appreciable. In certain extreme cases, where there are almost no germ nuclei present and the substance is greatly supercooled, the spontaneous nucleation throughout the volume will effect phase change. Such cases may be treated by picturing them in terms of a very numerous and uniformly dense distribution of germ nuclei with a correspondingly small $n(T)$, as will be seen below.

The variation of $A(T)$ with temperature has been worked out by Borelius[17] and Becker[18] for solid-solid reactions of a certain type. The form of this variation is probably quite general. A is found to decrease very rapidly as T is lowered, finally leveling off to an almost constant value at low temperatures. Q, on the other hand, is generally constant for a given substance over a large range. The result of the operation of these two factors is that, as the temperature drops, n increases from a negligible value at the critical temperature to a maximum at some subcritical temperature and then decreases again. A plot of $\lg 1/n$ against $1/T$ in a typical instance is indicated in Fig. 2. The two terms $A(T)/RT$ and Q/RT, as well as their sum, are separately indicated. As we shall later see, the importance of this chart is that, in certain common circumstances, it represents the temperature-time relation for a given degree of transformation of a substance, e.g., that represented in other coordinates in Fig. 1.

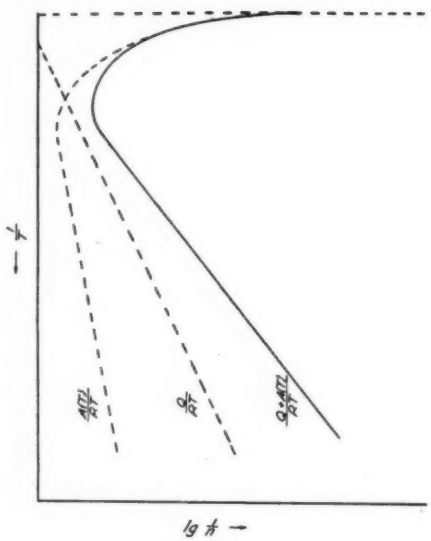

FIG. 2.

The second way in which germ nuclei can get used up is through being swallowed by growing grains of the new phase, and thereby rendered inoperative for growth themselves. If we let the number per unit volume thus ingested up to time t be designated by $N''\equiv N''(t)$, we have during any short time interval dt (and, as always in statistical laws, for the N's not too small)

$$dN=-dN'-dN'', \tag{1}$$

where

$$dN'=nNdt \tag{2}$$

and

$$dN''=\bar{N}dV. \tag{3}$$

dV is the increase in time dt of the volume of the new phase per unit volume of space. It might be thought that (1) should be further corrected by subtracting from dV, in the second term (dN''), the contribution made by the dN' growth nuclei formed in dt, since these have already been allowed for by the first term.

[16] I. N. Stranski and R. Kaischew, Zeits. f. physik. Chemie **B26**, 317 (1934); Physik. Zeits. **36**, 393 (1935).
[17] G. Borelius, Ann d. Physik **33**, 517 (1938).
[18] R. Becker, Ann. d. Physik **32**, 128 (1938).

* Since, as the work of Volmer (reference 11) has shown, the growth of crystals is primarily governed by the appearance of two-dimensional nuclei of the right size on the faces of the crystal, an expression very similar to the one for $n(T)$ results for the dependence of the rate of grain growth G on temperature.[16] In fact, we shall see later that there is strong evidence that, for a given crystallizing substance, n and G are approximately proportional to each other. This is extremely important in enabling us to simplify the treatment of phase changes under conditions of changing temperature and concentration.

It is, however, easy to verify that this correction is of the order $(dt)^3$ and therefore negligible by comparison with the other terms which are of the order dt.

Looking at (1), (2), and (3) we see that the total number of effective growth nuclei which appear throughout the phase change will depend upon the temperature of supercool because this alters the relative number of germ nuclei used for growth and those swallowed up. If we consider the case where n is relatively so large that almost all of them start growing before any ingestion can occur, the second term in (1) may be neglected by comparison with the first and we get

$$dN/dt = -dN'/dt = -nN. \qquad (1')$$

Therefore, for n constant with time (i.e., under conditions of constant temperature and concentration), $N = \bar{N}e^{-nt}$. The number of growth nuclei at time t would be

$$N' = \int_0^t nN dt = \bar{N}(1 - e^{-nt})$$

and the total number appearing $\bar{N}' = \bar{N}$. This does not give the dependence upon temperature of supercooling of the upper limit of the number of growth nuclei. But we can get a rough indication of the effect of varying supercooling temperatures upon the beginning of the process. If $n(T)$ is large, as it is for lower T, t can be still fairly small when an appreciable number of growth nuclei appear. Hence we get earlier intersection upon the abscissa and steeper slopes of the nuclei-time curves for lower, i.e., more critical supercooling. This is in general accord with experiment. Comparisons with the more exact theory will be given later.

If the other extreme be taken where n is small and the germ nuclei are so numerous and densely packed that the number which become activated for growth can be neglected by comparison with those which become ingested, (1) becomes

$$dN/dt = -dN''/dt = -\bar{N}dV/dt \qquad (1'')$$

and in the resultant formulae we have to put $N \to \infty$ $n \to 0$ $nN \to$ a finite rate of spontaneous nucleation per unit untransformed volume. This is equivalent to the Göler-Sachs assumption, and it is thus seen that the latter's analysis is included in ours as an approximation which is valid only in certain special cases.

It is convenient to simplify the analysis of (1) and (2) in the general case by changing the unit of time so that

$$ndt = d\tau \quad N(t) \to N(\tau) \quad V(t) \to V(\tau). \qquad (4)$$

In this way we get, by substituting (2) and (3) in (1),

$$dN/d\tau + N(\tau) + \bar{N}dV/d\tau = 0$$

which when integrated gives

$$N(\tau) + \int_0^\tau N(z)dz = N(\tau) + N'(\tau) = \bar{N}[1 - V(\tau)],^* \qquad (5)$$

an expression which is valid only up to $\tau = \bar{\tau}$, corresponding to $t = \bar{t}$ when the germ nuclei are exhausted and the number of growth nuclei becomes constant. At that moment $dV/d\tau$ may still be different from zero and so also $dN/d\tau$. But N becomes and remains zero and the relation derived from (1) can no longer be used. V can then be found from the functional $V|[N(\tau)]|$ as explained below.

In case n varies with time according to some known dependence $n(t)$ we may still make the substitution (4) with

$$\int_0^t n(y)dy = \tau,$$

and (5) is again valid though the unit in which we measure time is variable; i.e., it is itself a known function of the time depending upon the nature of the substance and how we vary its environment (e.g., temperature or concentration) during phase change. We may call the time scale defined by (4) the *characteristic time scale* of the substance and process. The phenomena, as described in it, may be called the *characteristic phenomena*. From now on, unless otherwise specified, we shall use this characteristic time which has the effect of removing n from our formulae. We shall later (Section D) see an additional very remarkable consequence of the introduction of the characteristic time scale.

* We may note that in the case where the nuclei are distributed solely upon a surface S, considerations similar to the foregoing may be carried through and we get an equation like (5) but with $V(\tau)$ replaced by $S(\tau)$. The theory will be dealt with in a subsequent paper.

The functional equation (5) relating N and V may be described physically as follows: $1-V(\tau)$ is the yet untransformed volume (per unit volume of space) at time τ, and $\dot{N}[1-V(\tau)]$ the corresponding number of germ nuclei *had these retained their original density*. But, since the (changing) untransformed volume has been drained throughout its history by spontaneous growth nuclei forming to the total extent of $N'(\tau)$, we must subtract the latter from $\dot{N}[1-V(\tau)]$ to get the number of still effective germ nuclei.

Besides (5) we may find another relation between V and N, in that V is a *functional* $V|[N(\tau)]|$ of N (in the sense of Volterra[19]), i.e., at any time τ, it depends upon the values of $N(\tau)$ throughout the interval 0 to τ. Like any analytic functional, V can be represented in a Taylor-like expansion by a series of simple functionals (integrals), the first linear, the second quadratic, etc. In the next section we shall see the simple physical interpretation of these terms. When computed, the expression for $V|[N(\tau)]|$ may be inserted into (5) and the resultant functional equation determines $N(\tau)$. From this, $N'(\tau)$ and $V(\tau)$ are readily computed, and the kinetics of the transformation found. We shall illustrate by various cases in the following papers.

C. Geometry and Kinetics of a Crystal Aggregate

We may easily see the physical significance of the various order terms in the expansion of $V|[N(\tau)]|$ by considering the geometry of a crystal aggregate. We shall first derive some general relationships which will be independent of any assumptions about the distribution of the centers of the grains. Later we may specialize this distribution in various ways corresponding to important physical situations.

Suppose, at any fixed time, we consider an aggregate of grains of various shapes and sizes, the result of growth from centers beginning at various times in the past. The assumption we make is that where one grain impinges upon another growth ceases.* We may denote by the adjective "extended" the volume of any grain had its growth been unimpeded by impingement upon any other grain. Let the volume at time τ of any grain which began growth from a nucleus (of negligible size) at time z be $v(\tau, z)$. The number of such grains beginning at z is given by $N(z)$. Thus the total extended volume (per unit volume) at time τ, which is the total transformed volume if we neglect overlapping of growing grains, is

$$V_{1\,ex}=\int_0^\tau v(\tau, z)N(z)dz. \tag{6}$$

This then is the linear term in the expansion of the functional $V|[N(\tau)]|$. For any particular case (e.g., constant linear growth) and shape of grain, an explicit function may be inserted for $v(\tau, z)$. We shall give examples later.

We may think of the actual pattern of grains of the new phase as made up of the extended grains overlapping each other in various groups, the overlapped regions being counted only once in getting the transformed volume $V(\tau)\equiv V_1$. Let V_1' denote the total transformed volume lying solely in the single grain (or nonoverlapping) regions of the extended volumes. This is indicated by dotted areas for a group of spherical grains in Fig. 3. Similarly let V_2' denote the transformed volume lying solely in double grain regions

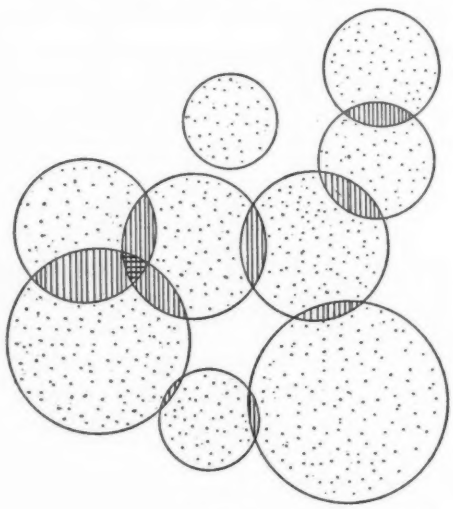

Fig. 3.

[19] V. Volterra, *Theory of Functionals* (Blackie and Son, London, 1930).

* This is usually true for cystalline growth. In other cases, as for instance in the condensation of vapor where there is coalescence of the liquid drops which are the "grains" of the new phase, the analysis would have to be modified accordingly.

(singly hatched areas), V_3' in triple grain regions (doubly hatched areas), and so on. Since each V_m' should be counted m times to get $V_{1\,ex}$ we have

$$V_{1\,ex}=V_1'+2V_2'+\cdots mV_m'+\cdots, \quad (7)$$

whereas the actual transformed volume

$$V_1=V_1'+V_2'+\cdots V_m'+\cdots. \quad (8)$$

(7) and (8) n be seen to be special cases of a more general set of relations as follows. Let the total volume of overlapping of all groups of k grains counted and added separately without regard to higher overlapping be designated $V_{k\,ex}$. Thus, for instance, in Fig. 3 $V_{2\,ex}$ is the sum of the singly hatched areas and three times the doubly hatched areas (plus six times the triply hatched areas, etc., in the case of higher overlapping). In general $V_{k\,ex}$ is equal to a sum of terms in which V_m' is multiplied by the number of combinations of m things taken k at a time. Thus

$$V_{k\,ex}=\sum_{m=k}^{\infty} C_k{}^m V_m' = \frac{1}{k!}\sum_{m=k}^{\infty} m(m-1)\cdots(m-k+1)V_m', \quad (7')$$

of which (7) is a special case. On the other hand, let V_k denote the total volume of overlapping of all groups of k grains where each element of volume is counted only once. In Fig. 3 V_2 is merely the sum of the singly hatched areas and the doubly hatched areas (plus the triply hatched areas, etc.) taken only once. In general

$$V_k=\sum_{m=k}^{\infty} V_m'. \quad (8')$$

It is $V_1\equiv V(\tau)$ which we wish to determine and, since it is the $V_{k\,ex}$ rather than V_k' that are most easily determined from statistical or other considerations (see below), we should like to get an expression for V_1 in terms of the $V_{k\,ex}$. Supposing that this is of the form

$$V_1=\sum_k A_k V_{k\,ex},$$

we may easily determine the coefficients A_k by substituting from (7') and comparing with (8). We find

$$A_k=(-1)^{k+1}$$

and therefore

$$V(\tau)\equiv V_1=V_{1\,ex}-V_{2\,ex}+V_{3\,ex}-\cdots+(-1)^{m+1}V_{m\,ex}+\cdots, \quad (9)$$

an expression for which it is not difficult to give an intuitive justification, e.g., in writing $V_{1\,ex}$ instead of V_1 we add 1 superfluous V_2' and 2 superfluous V_3'; by subtracting $V_{2\,ex}$ we compensate for the superfluous V_2' but overcorrect for the V_3's since there are $3V_3'$ in $V_{2\,ex}$; therefore we must add another $V_{3\,ex}$, but this requires further correction, etc. Again, (9) is a special case of a general formula for the V_j in terms of the $V_{k\,ex}$. Setting

$$V_j=\sum_k A_k{}^j V_{k\,ex}=\sum_{k,\,m} A_k{}^j C_k{}^m V_m'$$

and comparing with (8'), we may determine the coefficients $A_k{}^j$, and we get

$$V_k=\sum_{k=j}^{\infty}(-1)^{k-j}C_{j-1}{}^{k-1}V_{k\,ex}. \quad (9')$$

Similarly, by inverting (7'), or else by using the relation derivable from (8')

$$V_m'=V_m-V_{m+1}$$

in conjunction with (9'), we may express the V_m' in terms of $V_{p\,ex}$

$$V_m'=\sum_{p=m}^{\infty}(-1)^{p-m}C_m{}^p V_{p\,ex}. \quad (10')$$

Formulas (7'), (8'), (9'), (10'), or their equivalents, may very likely be derivable alternatively to the above, from probability considerations. We shall not attempt such a discussion here.

(9) may be regarded as the expansion of the functional $V|[N(\tau)]|$. Let us study the structure of the general term $V_{m\,ex}$ in greater detail. This will enable us to draw a very important conclusion. Let r, the "radius," be a measure of the linear dimensions of a grain. In case the growth is not purely radial but takes place by varying amounts in different directions so that the grain is not spherical, r may be regarded as a representative or suitably averaged quantity over the various directions. Similarly let G be the direction averaged rate of growth of r, in general varying with time due to changes in temperature, concentration, etc. Then r, at *ordinary* time t, of a grain

which began growth at *ordinary* time y is given by

$$r(t, y) = \int_y^t G(x)dx$$

or, if we introduce the characteristic time through the transformations

$$ndx = du \quad \tau = \int_0^t n(x)dx \quad z = \int_0^y n(x)dx,$$

$$G(x) \rightarrow G(u), \quad r(t, y) \rightarrow r(\tau, z),$$

we get

$$r(\tau, z) = \int_z^\tau \frac{G}{n} du \equiv \int_z^\tau \alpha du, \tag{11}$$

where we have introduced the function α for G/n. The grain volume is

$$v(\tau, z) = \sigma r^3 = \sigma\left[\int_z^\tau \alpha du\right]^3, \tag{12}$$

where σ is a shape factor. equal to $4\pi/3$ for a sphere.

Let us represent by $v(r_1, \cdots r_m, x_{12} \cdots x_{ij} \cdots)$ the volume of overlapping of m grains of "radii" $r_1, r_2, \cdots r_m$, when the centers of grains 1 and 2 are at distance x_{12} apart, of 1 and 3 at x_{13} apart, of i and j at x_{ij} apart, etc. If this volume is multiplied by the probability $D(r_1, \cdots r_m; x_{12} \cdots x_{ij} \cdots)$ of m such grains (of radii $r_1, \cdots r_m$) being found with mutual distances $x_{12}, \cdots x_{ij}, \cdots$, and integrated over all possible values of x_{ij}, we get the average volume of intersection of m grains of the given radii.

$$\bar{v}(r_1, \cdots r_m) = \int \cdots \int v(r_1, \cdots r_m; \cdots x_{ij} \cdots)$$

$$\times D(r_1, \cdots r_m; \cdots x_{ij} \cdots) dx_{12} \cdots dx_{ij} \cdots. \tag{13}$$

The form of the function D will naturally depend upon the distribution of the grain centers. For any particular type of distribution and grain shape, it may be worked out explicitly from statistical considerations, and $\bar{v}(r_1, \cdots r_m)$ may be evaluated.

Using (11), we have for the average volume of overlapping at time τ of m grains which began at times $z_1, z_2, \cdots z_m$

$$\bar{v}(r_1, \cdots r_m)$$

$$\rightarrow \bar{v}\left[\int_{z_1}^\tau \alpha du, \int_{z_2}^\tau \alpha du, \cdots \int_{z_m}^\tau \alpha du\right] \equiv \bar{v}_m, \tag{12'}$$

which may be regarded as the generalization of (12). The total number of overlappings due to grains starting during (characteristic) time intervals dz_1, dz_2, $\cdots dz_m$ is $N(z_1)N(z_2)\cdots N(z_m)dz_1dz_2\cdots dz_m$ where, so as not to count any m'th order overlapping more than once, we shall set $z_1 > z_2 > \cdots > z_m$. The total extended volume of overlapping at τ is then

$$V_{m\,\mathrm{ex}} = \int_0^\tau N(z_1)dz_1 \int_0^{z_1} N(z_2)dz_2 \cdots$$

$$\times \int_0^{z_{m-1}} N(z_m)\bar{v}_m dz_m, \tag{6'}$$

which may be regarded as the generalization of (6). It is now evident that $V_{m\,\mathrm{ex}}$, and therefore the transformed volume V, in the characteristic time scale depends upon n and G only through the ratio α. This permits us to draw a very important conclusion as we shall see in the following section.

D. Invariance of the Characteristic Phenomena in the Isokinetic Range. Temperature-Time Curves

The factors which govern the tendency of the growth nuclei to grow out of the germ nuclei are similar to those which govern further growth, i.e., we may expect the variation of n and G with external conditions to be similar. As we have mentioned above, this is borne out in the special cases which have been worked out by the resemblance of the formulae for the two quantities.[11, 16]

It is thus plausible from our picture of the underlying mechanisms that n and G are approximately proportional throughout a considerable temperature and concentration range. Let us designate this the *isokinetic range*. We shall see below that the consequences of assuming the existence of an isokinetic range are well verified in experiment and explain some otherwise purely empirical observations.

If, therefore, we suppose that

$$G/n \equiv \alpha$$

is a constant for a given substance in the isokinetic range, we may write from (11) and (12)

$$r = \alpha(\tau - z), \tag{14}$$

$$v(\tau, z) = \sigma\alpha^3(\tau - z)^3 \tag{15}$$

and from (6),

$$V_{1\,ex}=\sigma\alpha^3\int_0^\tau(\tau-z)^3N(z)dz. \qquad (16)$$

(6′) becomes

$$V_{m\,ex}=\int_0^\tau N(z_1)dz_1\int_0^{z_1}N(z_2)dz_2\cdots$$

$$\times\int_0^{z_{m-1}}N(z_m)\bar{v}[\alpha(\tau-z_1),\cdots\alpha(\tau-z_m)]dz_m \qquad (6'')$$

and since α is independent of temperature and concentration, so also is the relative internal history of the transformation and the description of the kinetics of the process in the τ language. Here we have the justification for calling the phenomena, so described, the characteristic phenomena. To restate: *For a given substance and crystal habit there is an isokinetic range of temperatures and concentrations in which the characteristic kinetics of phase change remains the same.* The only difference in the phenomena at one temperature (concentration) or another is in the size of the unit of time. If the temperature (concentration) is varying during the phase change (nonisothermal), the description is still the same in terms of τ, but the unit of measure of τ in terms of t is variable during the process, and this must be watched in translating the description of the phenomena from the τ language to the t language. Thus, to lay the foundation for the solution of the entire range of reaction kinetics problems, we need to solve only the one problem in the τ language. We shall now examine some of the experimental consequences.

If the transformed volume for a given substance and grain shape is a function solely of τ then we may expect a parallelism of reaction curves taken at different constant temperatures and concentrations and plotted on a logarithmic *ordinary* time scale. This follows from the relation $\tau=nt$ whence

$$\lg t=\lg\tau-\lg n.$$

In other words, the $\lg t$ scale, on which each curve is separated from every other, is shifted from the single common master $\lg\tau$ scale by the temperature (concentration) dependent parameter n. The shift-coincidence, as we may call it, of reaction curves at constant temperature and concentration on a $\lg t$ scale has been indicated here and there in the literature without its origin being understood. The curves by Bain and Davenport[3, 20] on the isothermal decomposition of austenite in various C, Cr, Ni, and Mn steels clearly show this effect. Another way of stating the conclusion is that if we use as abscissa the time *relative* to some definite degree of transformation, e.g., $t_{0.5}$ for 50 percent transformation, i.e.,

$$t/t_{0.5}=\tau/\tau_{0.5}$$

we get a single curve on which lie all the points of the different isothermal reactions. Tammann[21] has given curves in which Bain's data are plotted in this way. Upton[22] has drawn a similar curve to represent the original data of Bain and Davenport[3] on carbon and Cr steels.

Looking at the relation

$$\lg t=\lg\tau-\lg n$$

in another way, we note that, for a given degree of transformation, $\lg t$ is proportional to $-\lg n$. In other words, on a $1/T-\lg t$ plot, the temperature-time curves should all have the same shape as the resultant curve in Fig. 2, being shifted from each other by the parameter $\lg\tau$. We note that, because $A(T)$ becomes nearly constant at lower temperatures, $(Q+A(T))/RT$ then approaches a straight line. This result of the theory, which should be expected to hold for any substance in its isokinetic range, has been discovered empirically for austenite decomposition in steels by Austin-Rickett[23] working with the data of Bain-Davenport. It thus constitutes additional evidence that the phenomena in this range are isokinetic. The general formula for the temperature-time curves will be considered in the subsequent papers.

Another consequence of the invariance of the phenomena on the τ scale is that since

$$\alpha=G/n=Gt/\tau$$

is a constant, and τ is the same at all temperatures for a given degree of transformation, e.g., $\tau=\tau_{0.5}$, independent of temperature, for $V=0.5$,

$$Gt_{0.5}=\alpha\tau_{0.5}$$

[20] E. C. Bain, Arch. Eisenhüttenw. **7**, 41 (1933).
[21] G. Tammann, Zeits. f. anorg. Chemie **214**, 407 (1933).
[22] G. B. Upton, Trans. A. S. M. **22**, 690 (1934).
[23] J. B. Austin and R. L. Rickett, Metals Technology, September, 1938, T.P. No. 964.

TABLE I.

TEMPERATURE °C	$t_{0.5}$ TIME IN SEC.	G RATE OF GROWTH IN CM/SEC.	$Gt_{0.5}$
717	30,000	$5\cdot10^{-8}$	1.5×10^{-3}
704	1050	$1.0\cdot10^{-6}$	1.05×10^{-3}
662	30	$3\cdot10^{-5}$	$.9\times10^{-3}$
620	4	$2.5\cdot10^{-4}$	1×10^{-3}
580	2	$5\cdot10^{-4}$	1×10^{-3}

should also be the same at all temperatures (in the isokinetic range). This conclusion is well verified by an examination of the work of Zimmerman, Vilella, and Guellich[24] on a eutectoid steel, from which Mehl[9] has calculated G approximately. The results, exhibited in Table I, show remarkably good agreement in the values of $Gt_{0.5}$ over the entire temperature range in which G itself varies ten thousand-fold. We shall later consider more detailed evidence for the constancy of α. In the meantime we merely emphasize that with its help the solution of the entire class of reaction kinetics problems of this type is reduced to the solution of Eqs. (5) and (9), using (6′).

We have seen that $V_{m\ \mathrm{ex}}$ involves m-fold integration with $N(z_1)N(z_2)\cdots N(z_m)$ as a factor in the integrand. For any particular type of grain growth the remaining factor may be worked out from statistical considerations and written explicitly. When the expression (9) or an approximation thereto for $V(\tau)$ is inserted in (5) the resulting functional equation determines $N(\tau)$. From this $N'(\tau)$ and $V(\tau)$ may be computed, and the kinetics of the transformation known. This procedure is a lengthy and difficult one to carry out in general. We shall illustrate it in one special case in a subsequent paper by using the approximation

$$V(\tau)=V_{1\ \mathrm{ex}}-V_{2\ \mathrm{ex}}.$$

Fortunately, when the distribution of grain centers is random, we may avoid detailed statistical considerations by using the general method to be developed in the following paper. Later we shall compare the results of the two methods in the aforementioned special case.*

In the subsequent papers we shall work out the kinetics of transformation for various cases where the regions of distribution of the germ nuclei are respectively the volume, internal surfaces of the old phase, and both the volume and surfaces. In general we find good agreement with the voluminous experimental data as well as additional insight into the physical processes involved.

The author wishes to acknowledge his indebtedness to Dr. E. R. Jette of Columbia University for much helpful discussion.**

[24] J. G. Zimmerman, J. R. Villela, and G. E. Guellich, Metals and Alloys **22**, January, 1937.

* We may again emphasize that the considerations we have hitherto advanced are independent both of the manner in which the germ nuclei are distributed and the dimensionality of the regions considered, i.e., if the nuclei are distributed upon a surface S the V symbols throughout may be replaced by S symbols with analogous interpretations.

** *Note added in proof.*—Upon further consideration, it seems that (3) and therefore (5), should be replaced by a more accurate relation which also turns out to be simpler in its consequences. In (3) we have assumed that the number of germ nuclei per unit volume which the advancing front of the new phase encounters is the original density $\bar{N}$. But it will be seen that this is a valid approximation only when the density of growth nuclei is small compared with the density of germ nuclei. Otherwise, the actual density encountered, on the average, by the advancing front of the new phase is $N/1-V$, where $1-V$ is the fraction of untransformed volume per unit volume. (3) then should be replaced by

$$dN''=\frac{N}{1-V}dV \tag{3′}$$

which, substituted into (1), gives

$$\frac{dN}{dt}=-nN-\frac{N}{1-V}dV.$$

Integrating, and introducing the characteristic time, we have instead of (5)

$$N(\tau)=\bar{N}e^{-\tau}[1-V(\tau)] \tag{5′}$$

and the density of growth nuclei as a function of the time is given by

$$N'(\tau)=\bar{N}\int_0^{\tau}e^{-z}[1-V(z)]dz. \tag{5″}$$

An important result of this correction is that N drops off asymptotically to zero instead of vanishing of itself for some finite value of the time. To keep a correspondence between the statistical theory and experience when N becomes small, we should, however, assign a definite exhaustion time $\bar{\tau}$ when N becomes of the order of unity, i.e.,

$$N=1=\bar{N}e^{-\bar{\tau}}[1-V(\bar{\tau})].$$

Beyond $\bar{\tau}$, N is taken to be zero and N', a constant, equals

$$\bar{N}'=\bar{N}\int_0^{\bar{\tau}}e^{-z}[1-V(z)]dz.$$

$N/1-V$ and $\bar{N}$ are very nearly equal if N' (or n) is relatively small, and therefore the considerations in the limiting cases (1′) and (1″) remain unchanged. The subsequent discussion concerning the functional dependence of V upon N also remains unchanged.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Inertial Effects in the Skeletal Vibrations of Tetramethylmethane and Tetramethylsilicon

In a letter to this journal, Wall and Eddy[1] reported some calculations on the vibrational frequencies of tetramethylmethane and tetramethylsilicon. They assumed that there are certain modes in which each methyl group moves as a single particle of mass 15, and that these can be determined by treating the molecules as tetrahedral XY_4 systems. They found, however, that the X–Y force constant obtained from this approximate treatment was notably smaller than the corresponding value they had used in an exact treatment of the totally symmetric nondegenerate modes of these molecules.

The reason for the discrepancy is that in replacing the methyl group by a particle of mass 15 no account is taken of the motions of the hydrogen atoms relative to the carbon atom. Since the sum of the hydrogen masses is a considerable fraction of the mass of the radical, their motions are sufficiently large in the skeletal modes to introduce inertial effects which alter the effective mass of the group. The nature of this correction is easily determined for the nondegenerate skeletal mode by an exact treatment of the nondegenerate modes of the complete molecule. When the latter is carried out it is found that the lowest mode may be regarded as one in which the methyl group moves as a unit and that the frequency is that of a mass *greater* than 15 vibrating under the X–C force constant. From the known amplitudes of the hydrogen and carbon atoms this mass is readily determined. It is of interest to note in passing that the correction is less in the case of tetramethylsilicon than in tetramethylmethane due to the fact the Si–C force constant is less than that of the C–C bond. We observe that as the X–Y constant approaches zero we approach a mode in which the methyl group undergoes a rigid translation, and its effective mass is simply 15.

TABLE I.

TETRAMETHYLMETHANE		TETRAMETHYLSILICON	
OBS.[2]	CALC.	OBS.	CALC.
733 cm^{-1}	733 (1)	598 cm^{-1}	598 (1)
414	414 (2)	239	239 (2)
335	343 (3)	202	228 (3)
925	904 (3)	863	861 (3)
$k_{XY}=5.18\times10^5$ dynes/cm		$k_{XY}=3.31\times10^5$ dynes/cm	
$k_\vartheta=0.551\times10^5$ dynes/cm		$k_\vartheta=0.176\times10^5$ dynes/cm	
$k_{Y\vartheta}=1.04\times10^5$ dynes/cm		$k_{Y\vartheta}=0.437\times10^5$ dynes/cm	
$M_{eff}=16.3$		$M_{eff}=15.7$	

On the assumption that the inertial effect on the degenerate modes is in the same direction as in the nondegenerate mode, I have calculated the skeletal frequencies of these molecules, considering them as XY_4 systems. I used a simple valence force potential plus an interaction term. Of the various functions tried, the one giving the best results is

$$2V=k_{X-Y}\sum_i \delta r^2_{X-Y_i}+k_\vartheta \sum_{\text{pairs}} \delta\vartheta^2_{Y_i-X-Y_j} +2k_{Y\vartheta}\sum_{\substack{\text{pairs}\\ ij}} \delta\vartheta_{ij}(\delta r_i+\delta r_j).$$

The stretching constant k_{X-Y} was taken from the exact treatment by Wall and Eddy referred to previously. k_ϑ was determined from the doubly degenerate mode and $k_{Y\vartheta}$ was then adjusted to give the best agreement in the triply degenerate modes. The frequencies and the assigned multiplicities are given in Table I.

The agreement is quite satisfactory in view of the fact the mass is taken the same in the degenerate modes as in the nondegenerate mode. Each case must be considered separately. A more detailed study will be presented in the near future.

I wish to express my thanks to Professor Slater for helpful discussions and criticisms.

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Cambridge, Massachusetts,
October 27, 1939.

[1] Wall and Eddy, J. Chem. Phys. **6**, 107 (1938).
[2] Rank and Bordner, J. Chem. Phys. **3**, 248 (1935).

Erratum: Changes of Phase and Transformations of Higher Order in Monolayers

(J. Chem. Phys. **7**, 931 (1939))

Two lines of Table I on page 940 have been omitted, and should read

	T_{cc}	AREA AT P	AREA AT M	$V^{2/3}$ (CALC)
Elaidic Acid C_{18}	25°	28–30	57	64
Tariric Acid C_{18}	<0°	28–30	58	64.

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Cambridge, England,
November 10, 1939.

On The Nature of The Liquid State

The most successful attempts, empirically, at developing a theory of liquids in terms of van der Waals forces, are based on the concept of a free volume of atomic dimensions in which each molecule is free to wander under the influence only of its nearest neighbors.[1] Essentially this is an artificial device to permit the use of a gas type of partition function, while at the same time ensuring that the external pressure on the assembly needs to have only small values compared with those which would be required to keep a gas at the same density.

There is a classical and theoretically much more acceptable device for accomplishing exactly this result, namely the intrinsic pressure of Laplace.[2] In modern language, the van der Waals forces build up a potential well within the liquid. Using methods familiar in metal theory, this well can be smoothed out, leaving only the potential wall at the boundary. Within this wall the molecules are free to behave as a gas of spheres with non-negligible size. Only those molecules whose kinetic energy is greater than the height of the wall will contribute to the external pressure.

Assuming the van der Waals forces are similar to those found by Lennard-Jones,[3] the mean potential per molecule will rise with increasing temperature because greater kinetic energy will carry molecules further up into regions of positive potential of interaction with its neighbors. But there exists for these forces an optimum density at which the potential has a greatest depth. If T_c is the temperature at which for this optimum density the mean potential per molecule just vanishes, then for T greater than T_c no density can be found for which the potential is negative. The liquid cannot exist as a separate phase at such temperatures.

For T less than T_c it is always possible to find a density near enough to the optimum value to form a potential well in which at least some of the molecules can be trapped by what is thus equivalent to an intrinsic pressure.

If the liquid is in contact with its own vapor, the saturated density of the latter can easily be calculated as an equilibrium problem. The liquid density has to adjust itself to the vapor pressure, reacting as a gas to the sum of this pressure and the intrinsic pressure.

The liquid-vapor change on this picture is consistent with Mayer's rigorous treatment,[4] and with the clustering picture developed since.[5] The present picture illuminates the process of freezing as follows. The liquid phase exists when the density is such that the van der Waals forces integrate to produce a potential well in which the molecules can float as units. At greater densities, the molecular collisions become so intimate that the electron shells are seriously disturbed. Finally there will be a critical density at which the coupling between the molecular core and the outer shell is broken; there will then be a sudden transition from intramolecular coupling between core and shell, to intermolecular coupling between cores on the one hand and shells on the other. This gives the picture of the crystalline state developed by Shockley,[6] in which the cores float as a lattice in a potential well caused by the charges on the electron gas.

The detailed analysis required for the complete elucidation of this picture of the liquid state is now being undertaken.

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Peiping, China,
September 26, 1939.

[1] Lennard-Jones and Devonshire, Proc. Roy. Soc. **A165**, 1 (1938); Kincaid and Eyring, J. Phys. Chem. **43**, 37 (1939).
[2] Lord Rayleigh, *Scientific Papers*, Vol. III, Article 176.
[3] Lennard-Jones and Devonshire, Proc. Roy. Soc. **A163**, 53 (1937).
[4] J. Mayer, J. Chem. Phys. **5**, 67 (1937); **6**, 87 (1938).
[5] W. Band, J. Chem. Phys. **7**, 324 (1939).
[6] W. Shockley, J. App. Phys. **10**, 543 (1939).

The Heat Capacity of Cyanogen Gas

We have determined the heat capacity of cyanogen gas using the adiabatic expansion method of Lummer and Pringsheim. Pure nitrogen was used as the standard comparison gas, its heat capacity being calculated from spectroscopic data. Two different samples of cyanogen were used, each of which was prepared from copper sulphate and potassium cyanide. Care was taken to free the gas from hydrogen cyanide, water, and carbon dioxide. In Table I the experimental molal heat capacities at constant pressure, obtained at three different temperatures, are given. The values of C_P^0 are those for the gas at infinite attenuation.

The theoretical heat capacities in column three were calculated from the vibrational frequency assignment of Woo and Badger,[1] which gives the following values for the frequencies: $\nu_1=860$ cm^{-1}, $\nu_2=2150$ cm^{-1}, $\nu_3=2336$ cm^{-1}, $2\delta_1=230$ cm^{-1}, and $2\delta_2=512$ cm^{-1}. This assignment is in accord with the entropy data of Ruehrwein and Giauque,[2] and, as pointed out by Stevenson,[3] the frequency ν_1 is in agreement with the electron diffraction studies of Pauling, Springall and Palmer.[4] Eucken and Bertram,[5] as a result of their heat capacity measurements by the hot wire method, assigned a value of 740 cm^{-1} to the $2\delta_1$ vibration, but this value is certainly too high. The lower value, 230 cm^{-1}, has been confirmed recently by the work of Bailey and Carson[6] on the infra-red spectrum of the gas.

In the calculation of the experimental heat capacities $P=RT/(V-B_0)$ was used as the equation of state. The virial coefficients B_0 were calculated from the relation $B_0P_c/T_c=\beta_\theta-A/\theta-C/\theta 3$ given by Keyes,[7] where $\theta=T/T_c$. The values of the constants β_θ, A_θ and C_θ used for cyanogen were assumed to be the averages obtained by Keyes from eleven different nonpolar gases. It must be remembered that the values of B_0 for cyanogen obtained in this way may be in error by as much as 20 percent. The true values of B_0 are probably numerically greater than those given by

TABLE I.

TEMPERATURE (°A)	C_P^0 OBSERVED (CAL./DEG.)	C_P^0 CALCULATED (CAL./DEG.)	PERCENT DEVIATION FROM THEORY
273.16	13.14±.02	13.18	−.31
296.36	13.46±.02	13.53	−.52
326.91	13.96±.02	13.95	+.07

the Keyes relation. This may well account for a part of the small discrepancies between the experimental and calculated values at the lower temperatures.

Recently Stitt[8] has communicated values of C_v^0 for cyanogen as obtained by an improved "hot wire" thermal conductivity method. His values are from 2 percent to 4 percent higher than those predicted by theory, but, like those presented here, they are in essential agreement with the theoretically predicted heat capacities. The values of C_v^0 obtained by Eucken and Bertram, on the other hand, are over 20 percent less than those reported by Stitt and by us, and a frequency of $2\delta_1 = 740$ cm^{-1} rather than 230 cm^{-1} was required to get agreement with theory.

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Pasadena, California,
October 28, 1939.

[1] S. C. Woo and R. M. Badger, Phys. Rev. **39**, 432 (1932).
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[5] A. Eucken and A. Bertram, Zeits. f. physik. Chemie **B31**, 361 (1935).
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[7] F. G. Keyes, J. Am. Chem. Soc. **60**, 1761 (1938).
[8] F. B. Stitt, J. Chem. Phys. **7**, 1115 (1939).

The Heat Capacity of Cyanogen Gas

The object of this note is to report three measurements of the heat capacity of cyanogen gas made several months ago on the "hot wire" thermal conductivity apparatus[1] at Harvard University. At that time it was intended to later study the infra-red spectrum of cyanogen and perhaps make more measurements of the heat capacity. Since this additional work has been indefinitely postponed, the earlier results are reported now.

The bracketing procedure already described[1] was employed. When a platinum black wire was used, it was found that the ratio of the thermal conductivity of cyanogen to that of ethylene under the same conditions was greater than with a bare platinum wire, whereas the opposite was found to be true when cyanogen was similarly compared to acetylene. This indicates[1] that the accommodation coefficient of cyanogen is intermediate between those of ethylene and acetylene, that is $\alpha_{C_2H_4} > \alpha_{C_2N_2} > \alpha_{C_2H_2}$. Upper and lower limits to the heat capacity of cyanogen found from the thermal conductivity data assuming that $\alpha_{C_2H_2} = \alpha_{C_2H_2}$ and that $\alpha_{C_2N_2} = \alpha_{C_2H_4}$ are shown in columns 2 and 3, respectively, of Table I. These values are for the gas at 0.01 mm pressure, or essentially for the ideal gas. Values of the heat capacity of acetylene were calculated using harmonic vibrational frequencies 612(2), 729(2), 1973, 3283, and 3372 cm^{-1}; values for ethylene were taken from Eucken and Parts.[2] The experimental error of the thermal conductivity data is believed to be less than 1 percent.

TABLE I. *The heat capacity of cyanogen gas.*

T (°K)	Experimental C_v^0 (cal./mole-degree)		Calculated C_v^0 (cal./mole-degree)
185.2	9.61	9.59	9.41
294.1	12.05	12.04	11.54
320.4	12.42	12.29	11.91

The values of the heat capacity of cyanogen reported in Table I are not at all in agreement with those found by Eucken and Bertram[3] by the "hot wire" method on the assumption that argon and cyanogen have the same accommodation coefficient. Recent adiabatic expansion measurements by Burcik and Yost[4] lead to values in essential agreement with those reported here, so there is little doubt that the earlier values are in error. This conclusion was also suggested by Woo[5] on the basis of force constant considerations.

A study of the available spectroscopic data[6] on cyanogen indicates that Mecke's assignment[7] of the fundamental frequencies is probably correct. The frequencies used in calculating the figures in column 4 of Table I are 230(2), 510(2), 850, 2150, and 2330 cm^{-1}. The last four of these are definitely established from the infra-red and Raman data and the selection rules. The value of the lowest frequency is the most doubtful, although its determination[6(c)] from the ultraviolet spectrum seems rather reliable. The calculated values of Table I differ from the experimental by considerably more than the estimated experimental error. It is not certain at present whether this disagreement is due to larger error in the experimental values or at least partly to an error in the calculated values. If the contributions to the heat capacity of all but the lowest of the frequencies are assumed to be correctly calculated using the harmonic frequencies listed, a contribution of slightly over 1.99 cal./mole-degree for the lowest frequency is needed to bring the observed and calculated values into perfect agreement at the higher temperatures. This suggests that the calculated values might be appreciably higher if anharmonicity could be adequately taken into account.

I wish to thank Mr. Debeau for preparing the cyanogen used in this work. It was prepared by the usual method.[8]

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October 21, 1939.

[1] G. B. Kistiakowsky, J. R. Lacher and F. Stitt, J. Chem. Phys. **7**, 289 (1939).
[2] A. Eucken and A. Parts, Zeits. f. physik. Chemie **B20**, 189 (1933).
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[5] S.-C. Woo, Zeits. f. physik. Chemie **B37**, 399 (1937).
[6] (a) W. Burmeister, Verh. dschen. physik. Ges. **15**, 589 (1913); (b) J. Strong and S.-C. Woo, Phys. Rev. **42**, 267 (1932); (c) S.-C. Woo and R. M. Badger, Phys. Rev. **39**, 932 (1931); Reitz and Sabathy, Monats. f. Chemie **71**, 131 (1938).
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[8] See G. B. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. **1**, 432 (1933).

* This work was done while the author was a National Research Fellow in Chemistry at Harvard University.

J. C. Hedgford

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